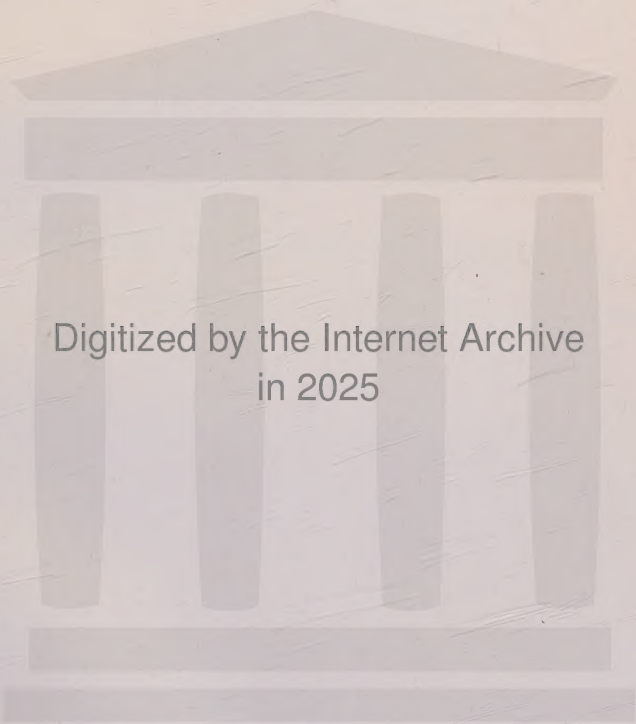


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THE EFFECTS OF MOISTURE ON CHEMICAL AND PHYSICAL CHANGES

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BY

J. W. SMITH, B.Sc., PH.D. (LONDON)

UNIVERSITY COLLEGE, LONDON

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PREFACE.

THERE is perhaps no more interesting and at the same time more puzzling group of phenomena than the chemical and physical effects produced by minute traces of water. It has been known for a long time that small quantities of water exercise a most important catalytic effect on the velocity of many chemical reactions, whilst the very interesting researches of Professor H. B. Baker and Professor A. Smits have drawn attention to the remarkable phenomena which appear when liquids and solids are subjected to a process of very intensive drying.

Dr. Smith has been engaged in my laboratory during the last few years on the investigation of the intensively dried system $\text{N}_2\text{O}_4 - \text{NO}_2$, and on the effect of intensive drying on the thermal dissociation of nitrogen dioxide. His interest, however, extended much beyond the actual substances which he studied experimentally, and led him to make a very complete search of the scientific literature connected with the effect of traces of water on physical and chemical reactions.

At my suggestion he undertook to write the present book, which I feel sure will be of great value to students and investigators who are interested in physico-chemical science. It is clear from recently published papers that the last word in connection with this group of phenomena has by no means been said, and that, in fact, we are just at the beginning of an understanding

of the extremely curious and puzzling facts so admirably and clearly set forth in the present work.

To the physical chemist the subject of catalysis is one of major interest and importance, and water seems to be undoubtedly one of the most important of these catalytic agents, whilst from the point of view of the physicist, the peculiar effects of intensive drying on the properties of solids and liquids urgently demand and require a close theoretical and experimental study.

Dr. Smith has shown himself to be admirably fitted for the task which he has undertaken, and I can warmly recommend his book to a very wide circle of readers.

F. G. DONNAN.

THE SIR WILLIAM RAMSAY LABORATORIES OF
INORGANIC AND PHYSICAL CHEMISTRY,
UNIVERSITY COLLEGE,
LONDON.

AUTHOR'S PREFACE.

IN this book an attempt is made to collect the data at present available concerning the effects of the removal of water vapour from chemical systems, and to correlate them in so far as is at present possible. As the technique of many of these investigations is of a highly specialised order, and numerous precautions need to be taken in order that positive results may be obtained, it has been deemed advisable to give considerable attention and space to this matter. Especially in the discussion of certain typical reactions which are retarded by desiccation, and in dealing with the influence of intensive drying on physical properties, the experimental procedures of the more characteristic investigations are given at some length. In all other cases an indication is given, wherever possible, of the mode of procedure employed in attaining the results described.

I desire to express my indebtedness to Dr. W. C. de Liefde of the University of Amsterdam, a copy of whose thesis, including a historical survey of this subject, was placed in my hands just before this book went to press. This brought several scattered references to my notice, and they have been embodied herein. My warmest thanks are also due to the proprietors of the following journals for permission to reproduce diagrams which have been published by them: *Journal of the Chemical Society*, *Journal of the American Chemical Society*, *Journal of Physical Chemistry*,

Zeitschrift für physikalische Chemie, Zeitschrift für anorganische Chemie, and Chemisch Weekblad.

In conclusion, mention must be made of the valuable assistance I have had from the editor of this series. It was at the suggestion of Professor Donnan that I began to write this book, and his helpful advice and kindly encouragement have been invaluable.

J. W. SMITH.

UNIVERSITY COLLEGE,
LONDON, *July*, 1929.

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THE EFFECTS OF MOISTURE ON CHEMICAL AND PHYSICAL CHANGES.

CHAPTER I.

INTRODUCTORY.

THAT the presence of a certain amount of water vapour is a necessary condition for the progress of many chemical reactions is a fact which has been known for a very long time, but it is only in comparatively recent years that any systematic study has been made of the subject. These more detailed investigations, however, have been confined to a comparatively small number of reactions, and a vast unexplored field still lies before the research worker who cares to take up this subject. The more recent work has shown that the problem is by no means so simple as appeared at one time to be the case. Although the effect of moisture on some reactions may be explained readily, there are a large number of cases for which no really satisfactory explanation has yet been put forward. In still more recent times, the epoch-making discoveries of Baker, showing the enormous influence of the most minute traces of moisture on physical properties, have given a further impulse to the problem, which is at present well to the forefront amongst chemical researches.

The relative degrees of drying to which the substances must be subjected in order to produce the effects described in the following pages differ greatly, they differ so widely, in fact, that it seems well-nigh impossible that they should all be phases of the same phenomenon. Thus it appears highly improbable that water catalyses the reaction between hydrogen and chlorine in the same manner as it does that between carbon monoxide and oxygen. Extremely rough desiccation of the latter gas mixture causes a very marked difference in the velocity of their combination, whereas very careful drying indeed is required to produce any effect in the case of a mixture of hydrogen and chlorine. Although reactions appear to fall into two or three classes in this

respect, it is by no means easy to decide into which groups certain reactions should be placed. Considerable further research is required before a satisfactory classification can be made. Hence, in the present state of our knowledge of this subject, it appears inadvisable to discriminate between different degrees of dryness, and the experimental data are collected here to cover as far as possible all cases where the effect of water on the progress of reactions, has been investigated, excepting such cases as reaction in aqueous solution, or where water is known to play a chemical rôle in the reaction. Thus such cases as the necessity of water for bleaching by means of chlorine are not included in this discussion.

It may be of interest to give here some values which have been obtained for the amount of moisture still retained by gases which have been dried "thoroughly" by contact with various desiccating agents. Dittmar and Henderson¹ found that air which had been dried by means of calcium chloride may retain 0.001 gram of water vapour per litre. Dibbitts² found that 308 litres of air dried carefully by means of sulphuric acid still gave up 0.07 mgm. of moisture to phosphorus pentoxide. Morley³ attempted to measure the absolute amount of moisture retained by a gas dried by means of sulphuric acid by making use of the fact that the equilibrium water vapour pressure over such a drying agent is independent of the pressure of the inert gas. Hence he passed moist air under pressure slowly through a series of sulphuric acid drying bottles, and then through a weighed apparatus in which it passed first through a bulb in which it was moistened and then was allowed to expand considerably. From there it was again passed through sulphuric acid drying tubes. The whole apparatus from the moistening tube to the drying tubes was weighed, and the volume of air passed was measured. The amount of sulphur trioxide carried off by the air was also estimated. Then if x litres of compressed air were expanded to y litres, and the amount of moisture introduced per litre be assumed to be equal to the amount leaving per litre, then the loss in weight of the apparatus is equal to the weight of sulphur trioxide carried over, together with the weight of water retained by $(y - x)$ litres. In this way he found that after passage of 1163 litres, the loss in weight was 2.4 mgms. After correcting for the sulphur trioxide carried over, this comes almost exactly to the same figure as was found by Dibbitts for

¹ *Proc. Roy. Soc. Glasgow*, **22**, 33 (1891).

² *Z. anal. Chem.*, **4**, 180 (1876).

³ *Amer. J. Sci.* (iii), **30**, 140 (1885).

the amount of moisture which air dried carefully by means of sulphuric acid gave up to phosphorus pentoxide, so the natural conclusion is that the amount of moisture left after passage through phosphorus pentoxide is very small indeed.

Morley has also attempted to estimate even this small amount.¹ As in the former case, air was compressed and dried, and introduced into the apparatus, where it was first moistened slightly, and then greatly expanded and dried by phosphorus pentoxide. In his first experiment, 726 litres were expanded to 2428 litres, the rate at which the gas left the apparatus being 70 litres per day. Although the excess volume was 1702 litres, the loss of weight was less than 0.05 mgm. In a second experiment, where 211 litres were allowed to expand to 2841 litres which issued from the apparatus at the rate of 75 litres per day, the excess 2630 litres caused a loss in weight of a little over 0.05 mgm. Thus the 4332 litres of gas in the two experiments together caused a loss of weight of only 0.0001 gram. This consisted of both the water vapour and the phosphorus pentoxide carried off. When Morley came to measure the amount of phosphorus pentoxide vaporised on the passage of a slow stream of gas through it,² he found that 900 litres of air carried forward 0.02 mgm. of phosphorus pentoxide. Hence the 4300 litres of the earlier work would carry over 0.1 mgm., just the amount found for water and phosphorus pentoxide together. As Morley states, however, the experimental error in these experiments must necessarily be very high, so it can only be deduced that the amount of moisture retained by 4300 litres of air dried by slow passage over a short tube filled with phosphorus pentoxide is less than 0.1 mgm.; whether it is a quarter, a tenth, or a hundredth of this amount cannot be deduced definitely from existing data.

Assuming that water vapour accounted for a quarter of this total amount, we find that there is only one water molecule remaining to every 10^7 molecules of other gases. This gas, however, is still quite "moist" from the point of view of many reactions, and it is evident that gas which has been dried by long standing over phosphorus pentoxide must contain a much smaller fraction of water molecules than this. Smits³ suggests that the fraction of water molecules in a very intensively dried system may be only 10^{-10} or even less.

Although a very large number of reactions, and these of extremely varying types, have been found to be influenced by the

¹ *Amer. J. Sci.* (iii), **34**, 199 (1887).

² *J. Amer. Chem. Soc.*, **26**, 1171 (1904).

³ *Chem. Weekblad*, **25**, 82 (1928).

presence of water vapour, we cannot yet generalise so far as to say that a trace of moisture must be present in order that any reaction may proceed. We cannot, in fact, cite any particular classes of reaction for which the presence of water is or is not necessary. In the relatively early days of this work, Traube considered that moisture was necessary for all oxidation processes, at all events at ordinary temperatures:—¹

“ . . . kein Körper bei gewöhnlicher Temperatur auf trocknen Sauerstoff zu wirken vermag.”

In this he was, probably unconsciously, quoting the ideas of Mrs. Fulhame of nearly a century before, but even in this class of reaction, which is, generally speaking, strongly retarded by even rough drying, we have the notable exception of the oxidation of mercury, which appears to be totally uninfluenced by the presence or absence of water vapour.

The arguments against the suggestion that all reactions may depend on catalysis by a minute trace of impurities have been summarised extremely well by Hinshelwood,² who takes the crucial points to be the following:—

(i) It is without any experimental evidence, since no homogeneous gas reaction with a simple unimolecular or bimolecular mechanism has ever been cited as an example of a reaction which is stopped in the absence of water vapour.

(ii) Direct disproof cannot be demanded; the maker of the assertion can always say that the gases were not yet pure enough.

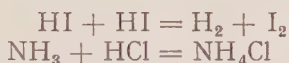
(iii) Indirect disproof is provided by the following facts. In reactions such as the decomposition of hydrogen iodide the maximum rate of reaction at a given temperature and pressure can be calculated from the kinetic theory of gases; it is equal to the total number of collisions between molecules with sufficient energy for chemical change. The observed rate is very nearly equal to this maximum possible rate. If the reaction could only take place when two molecules met in the presence of a third substance, the catalyst, present in exceedingly minute amount, then the observed rate would be vastly smaller than the maximum possible.

With reference to the particular case of traces of water acting as a catalyst, it is contended by Hinshelwood that the available data do not justify the conclusion that the reactions which take place much less readily in the absence of moisture would not

¹ *Ber.*, **18**, 1881 (1885).

² *School Science Review*, No. 31, 169 (1927).

occur quite readily in the absence of moisture at some higher temperature or pressure. He points out that if chemical combination between elements could not take place at all in the absence of water, all elements in the whole sidereal universe would be free to-day, since in the course of stellar evolution hydrogen and oxygen themselves would never have combined and made chemistry possible. He supposes that the induction that the retardation by drying is characteristic of all reactions is faulty. Although the reactions which have been shown to be inhibited by drying include combinations, dissociations, and double decompositions, the classification according to kinetic mechanism does not run parallel to these divisions. Thus although the reactions



might be expected not to differ in mechanism very markedly, they are actually quite different. The first takes place at a definite reproducible rate, varying continuously with temperature and pressure, and which has never yet been altered by drying. The second, under all ordinary conditions, is immeasurably fast; moderate drying produces no progressive slowing down, but if the gases and vessels are intensively dried, ammonia and hydrogen chloride may be mixed at ordinary temperature and pressure without any observable change at all.

In the case of the changes in physical properties on intensive drying, the branch of the subject which is dealt with in the later chapters, the position is vastly different. This does appear to be actually a general phenomenon. All the liquids and solids which have been so far investigated have shown some change in physical properties under very intense desiccation, the only negative results recorded having been obtained with substances which have been shown by other experimenters to show abnormal properties under these conditions.

The classification of the subjects treated in this volume is somewhat arbitrary in character. It is divided broadly into two sections, dealing respectively with the influence of moisture on chemical reactions and on physical properties, but even these two divisions merge into one another in some cases, as, for example, in the ammonium chloride problem. As far as possible, interrelated reactions are dealt with together in the place which has appeared to the author to be the most convenient for the purpose. Thus both the combination of silver oxide and carbon dioxide, and the dissociation of silver carbonate are discussed in

the section concerning Solid-Gas reactions ; the dissociation of ammonium chloride is dealt with among gaseous reactions in conjunction with the union of ammonia and hydrogen chloride ; whilst the system gold—chlorine—auric chloride is treated in the chapter dealing with the dissociation of solids, since it is only from this aspect that the latter system has been approached.

CHAPTER II.

GENERAL HISTORICAL SURVEY.

THE first direct mention of the effect of traces of water vapour on chemical reaction, so far as the present author is aware, was made by J. B. M. Bucquet, who, as early as 1780,¹ came to the conclusion that the presence of moisture was essential for the absorption of carbon dioxide by lime. (" . . . je conclus qu'il ne suffit pas de rendre à la chaux de l'air fixé pour la convertir en craie, qu'il faut un intermède pour cette union se fasse, et que cet intermède est de l'eau.") This deduction was drawn as a result of several careful experiments, and, indeed, it is practically all we know at the present day concerning the action of moisture in promoting the reaction between carbon dioxide and lime.

Several mentions of similar effects are also to be found in the works of Tobias Bergmann, who, at about the same time as Bucquet described his experiments to the Academie des Sciences, announced that arsenic did not tarnish in dry air.² He also mentioned that regulus of manganese when fused generally persisted in a dry place, but that in the presence of moisture it was soon oxidised and lost its lustre.³ Again, he noticed that water exerted a considerable effect on the spontaneous combustion of phosphorus. ("In vital air, without the aid of external heat, Phosphorus is consumed very slowly and scarce at all, unless water be present to forward the decomposition by a double attraction.")⁴

About the same period, Scheele, in his famous monograph entitled *Experiments on Air and Fire*,⁵ announced that pyrophorus did not oxidise in air which had been dried over quicklime,

¹ *Mem. Acad.*, **9**, 563 (1780).

² *Opuscula physica et chimica*, 1780.

³ *Physical and Chemical Essays*, English Trans., Vol. II., p. 204 (1786).

⁴ *Dissertation on Elective Attractions*, English Trans., p. 213 (1785).

⁵ English Trans. (1786), pp. 112, 130; cf. also *Creil's Annalen*, **1**, 483 (1786).

whereas it did so in moist air. Two passages are well worthy of quotation :—

“The water contained in common atmospheric air is the chief cause of the ignition of pyrophorus, whereof I shall speak afterwards.”

“I made a very dry air by putting some very small pieces of quicklime into a small matras; then I put the neck of another matras into that of the first so that the Air of both might communicate, and I luted the crevices with wax. Two days after, I separated the empty matras, and poured half an ounce of pyrophorus from my phial into it, and immediately carefully shut the aperture up; but I did not observe that it grew in the least warm. An hour after this, I put a sponge moistened in water into the matras and shut it again up: a few minutes after the pyrophorus began strongly to be heated and some pieces kindled spontaneously.”

Several examples of reactions for the progress of which the presence of moisture was necessary were also observed by William Higgins.¹ Such reactions included the interactions between phosphorus and oxygen, lime and hydrogen chloride gas, hydrogen sulphide and nitrous gas, and between iron and oxygen. Further details of his comments on these reactions are given later. Higgins was also the first experimenter to put forward a theory to explain the observed phenomena, and this theory was identical with the intermediate compound theory which was put forward independently by many other writers during the succeeding century. Discussing the influence of water on the oxidation of iron, he came to the following conclusion :—

“Hence it appears that iron has no effect on oxygen gas in a common temperature, and that it is the oxygen of the water which unites to it, while the oxygen of the gas is condensed by the liberated hydrogen in its nascent state so as to reproduce water. This is effected by a double influence which is so obvious as not to require an explanation. . . . The process of bleaching is effected in this way.”²

Following these observations came the very interesting work of Mrs. Fulhame.³ She found that if moist pieces of silk impreg-

¹ *Comparative View of the Phlogiston Theory* (1791); *Experiments and Observations on the Atomic Theory* (Dublin, 1814).

² *Comp. View*, p. 11; *Exper. and Obs.*, p. 52.

³ *Essay on Combustion, with a view to a new art of dyeing and painting, wherein the phlogistic and antiphlogistic hypotheses are proved erroneous* (1794).

nated with gold salts were exposed to the action of hydrogen, the salt was reduced and the material became gilded. If, on the other hand, the stuff were exposed to the hydrogen in a dry condition, this reduction did not occur. This she found to be a general property of cloths impregnated with salts of silver, gold, mercury, copper, lead, bismuth, and antimony, and of reduction by means of hydrogen, phosphorus, sulphur, alkaline sulphides, hydrogen sulphide, phosphine, and methyl iodide. Further, she observed that alcohol and ether had not the same effect as water in the promotion of this reduction. She came to the conclusion that the effect of moisture could not be to promote the reduction by breaking up the salt into minute particles, nor by condensing the gas and so bringing the hydrogen into closer contact with the metallic oxide, but, like Higgins, of whose work she appears to have been unaware, she supposed that there must be a double reaction :

“ . . . the water must be decomposed thus ; the hydrogen of the gas uniting with the oxygen of the water, whilst the hydrogen of the latter unites in its nascent state with the oxygen of the metal, reducing it and forming water.”

Mrs. Fulhame also considered that the observations of Bergmann and of Scheele indicated that water was necessary for all processes of oxidation ; indeed that water itself was the only oxidising agent.

“ Water is also decomposed in every instance of oxygenation, and the oxygen of the water alone oxygenates combustible bodies.”

“ Water is essential both to the reduction and oxygenation of bodies, and is always decomposed in these operations. . . . In every instance of combustion, water is decomposed and one body oxygenated by the oxygen of the water, whilst another is restored to its combustible state by the hydrogen of the same fluid.”

During the earlier part of the nineteenth century, several different investigators mentioned reactions which were totally stopped, or which were very much retarded, on the removal of moisture, but these researches were of a disconnected type, and each experimenter seems to have worked in ignorance of any previous investigations, so they did little towards building up a systematic knowledge of the subject. Thus Gilbert¹ found that dry lime did not absorb dry chlorine to form bleaching

¹ *Gilbert's Annalen*, 49, 315 (1815).

powder, and Cluzel¹ showed that the presence of moisture exerted a very pronounced influence on the reaction between hydrogen sulphide and sulphur dioxide. The former effect was observed also by several other investigators quite independently within the few succeeding years, but their quantitative results and their conclusions were very conflicting in character. A little later, Bonsdorff² demonstrated that atmospheric air, freed from carbon dioxide and moisture, did not tarnish clean surfaces of metallic potassium, arsenic, bismuth, lead, zinc, cadmium, iron, and copper; whilst Regnault³ showed that dry ethylene did not combine with chlorine in diffused daylight.

In 1841, Parnell⁴ once again drew attention to the important part played by water in chemical reactions:—

“The presence of water in the sphere of decomposition [produces] a force of considerable power, and one whose action has not been hitherto recognised. Its existence has been traced by observing the want of action of certain gases, and especially sulphuretted hydrogen, when in a perfectly dry state, on substances on which they exert a vigorous action in the presence of water. Thus papers impregnated with salts of lead, mercury, and copper were preserved from the action of sulphuretted hydrogen if rendered absolutely dry. That the effect of water in permitting action between these same bodies does not wholly depend on the diminution of the force of cohesion, by dissolving either the gas or the salt, is proved by several circumstances. First, this want of action is perceived only on particular salts; second, to restore the action, water may be present in a state of combination with the salt, and can then exert no solvent power; third, on moistening different dry salts with absolute alcohol, which dissolves six times its volume of sulphuretted hydrogen, and exposing to the gas, still no action ensued.

“On considering the nature of the salts on which the action of sulphuretted hydrogen is restrained, it appears that the function of water, in permitting action, is to combine with the acid, which should be rendered free by sulphuretted hydrogen immediately on its liberation. One equivalent of water is not in every case sufficient to satisfy the acid; for all anhydrous salts of the oxides of mercury, copper, or lead, can produce one equivalent of water with sulphuretted hydrogen.

¹ *Ann. Chim. Phys.*, **84**, 116 (1812).

² *Ann. Phys. Chem.*, **41**, 293 (1837); **42**, 325 (1837).

³ *Ann. Chim. Phys.* (ii), **69**, 171 (1838).

⁴ *British Association Report*, 1841, p. 51.

"The action of water may in some measure be assimilated to that between sulphuric acid of various degrees of strength and metallic iron or zinc. These metals, as is well known, undergo no change in oil of vitriol; while in this case, as well as when dry sulphate of lead is exposed to dry sulphuretted hydrogen, it would be said that all is present that is necessary to produce decomposition. But in both cases water must be added for action to ensue; in the one, to unite with the sulphate of zinc about to be formed, and in the other with the sulphuric acid. But there are some salts of those acids which are unacted on by sulphuretted hydrogen when dry, whose acid or hydracid of its salt radical possesses but little affinity for water, and consequently to which this explanation will not apply. In considering the cause of the want of action here, it must be remembered that sulphur is in reality a weak radical; that sulphuretted hydrogen is a compound which possesses great power over the results of chemical action, namely, insolubility of the sulphuret; and water being present, with which the acid can unite when free, it does not follow that decomposition must occur in one case because it does in another under the influence of other forces."

Parnell concluded by drawing an analogy between this phenomenon and the behaviour of caustic potash and calcium carbonate in the presence of only a small amount of water, when potassium carbonate and calcium hydroxide are formed. He considered that in this case the caustic potash had a greater affinity for water than the potassium carbonate, but that there was sufficient water to satisfy the demands of the carbonate, but not of the caustic potash, the result being that the former was produced.

In 1842, Andrews mentioned the influence of moisture on the reactions between chlorine and the heavy metals.¹ He had found that dry chlorine gas had no action whatever at ordinary temperatures on zinc, iron, or copper. On the other hand, the same dry gas instantly combined with arsenic, antimony, and phosphorus. Mercury was also found to combine slowly with dry chlorine.

About this same period, many investigators rediscovered the fact that dry alkali and alkaline earth oxides did not absorb carbon dioxide, but, owing to the lack of wide publicity, each appeared to be in entire ignorance of the work of the others. In 1847, Leconte² showed that dry nitric oxide and dry hydrogen

¹ *Trans. Royal Irish Academy*, **19**, 393 (footnote), (1842).

² *Ann. Chim. Phys. (iii)*, **21**, 180 (1847).

sulphide did not react, and Wilson,¹ a few years later, observed that dry hydrogen chloride did not redden blue litmus. In 1869, Wanklyn² observed that sodium could even be fused and shaken with chlorine gas without reaction occurring, but he did not mention that his chlorine was very dry, which must have been the case in order for this to be carried out. About the same time Dubrunfaut³ found that carbon was not burnt in dry air so readily as in moist.

These, and several other observations were made during the period 1780-1880, but, as has been stated already, all the observations were unrelated, and no single problem had been by any means thoroughly investigated. Each experimenter seemed to work in total ignorance of any previous work on the same system, as a glance at any of the earlier papers on the influence of moisture on the absorption of carbon dioxide by lime will reveal. Thus it cannot be said that the subject really commences until the investigations of Dixon on the union of carbon monoxide and oxygen, first published in the *British Association Report* for 1880. This work rapidly aroused the interest of chemists all over the world, and the importance of water vapour in promoting chemical reaction came to be generally recognised. Since that time, a considerable amount of attention has been directed at various periods to the investigation of the influence of traces of moisture on chemical reactions, especially as regards thermal and photo-chemical combinations, and somewhat more general theories have been evolved to account for this behaviour.

During the present century, an entirely new aspect of the subject has been opened up through the discovery by Baker that extremely careful desiccation can exert a very pronounced effect on the physical properties of liquids and solids. The historical development of this side of the subject will be dealt with fully in a later chapter.

¹ *Repert. Chim. Appl.*, **1**, 165 (1859).

² *Chem. News*, **20**, 271 (1869).

³ *Compt. rend.*, **73**, 1395 (1871).

CHAPTER III.

GASEOUS REACTIONS.

THE SYSTEM CARBON MONOXIDE—OXYGEN—CARBON DIOXIDE.

THIS system was the first to be investigated in any systematic manner, and, moreover, has engaged the attention of more chemists than any other system. It is characterised by the fact that comparatively rough drying is quite sufficient to produce marked effects, and hence it appears to be a very suitable system for commencing quantitative investigations of the effects of very small, but known, amounts of water vapour on chemical reaction.

It was observed both by Horstmann¹ and by Dixon² that the product obtained by exploding a mixture of carbon monoxide and electrolytic gas was affected by the presence of water vapour. Since at the temperature reached in the explosion the excess carbon monoxide reacted with the steam forming carbon dioxide and liberating hydrogen, the presence of water vapour appeared to increase the affinity of carbon monoxide for oxygen and diminish that of hydrogen. This was exactly the opposite effect to that of adding carbon dioxide before the explosion. Hence Dixon investigated the effect of moisture on the explosion of carbon monoxide and oxygen.

The Union of Carbon Monoxide and Oxygen—Dixon's Investigations.—In 1880, Dixon³ made the astounding discovery that when a spark from a Leyden jar was passed through a mixture of two volumes of carbon monoxide and one volume of oxygen which had been dried thoroughly by passage through tubes containing sulphuric acid, no explosion was caused. The same result was obtained when a little more oxygen was added. He observed that it was very difficult to dry the gases thoroughly enough to prevent the explosion under atmospheric pressure, but that by a reduction in pressure it was easy to show that a

¹ *Ber.*, **10**, 1626 (1877).

² *British Association Report*, 1880, p. 503.

³ *Loc. cit.*, *Phil. Trans.*, **175 A**, 617 (1884).

mixture of the dry gases would not explode under the influence of the spark, which mixture exploded readily on addition of a minutest trace of moisture.

If a dry mixture of two volumes of carbon monoxide and one volume of oxygen were drawn into a eudiometer and placed under a pressure of 250 mm. at 17° C., several powerful sparks from a Leyden jar could be passed without causing the gases to unite. If a rapid succession of sparks from a Ruhmkorff coil were then passed, the gases united at the first discharge, and burnt slowly down the tube. On further drying of the eudiometer, sparks from the coil did not ignite the mixture at 100 mm. or at 150 mm. pressure. At 200 mm. the platinum wires became red hot, showing that some local action was produced. Under 250 mm. the gases ignited, but the disc of flame took about three seconds to travel half a metre down the tube. More recent experiments have shown that exhaustive drying by means of sulphuric acid is sufficient to produce this slow movement of the disc of flame with the gas at atmospheric pressure.¹

Dixon also found that a mixture which had been standing for an hour over phosphorus pentoxide could be sparked from a Leyden jar without result, but a Ruhmkorff coil caused ignition. A mixture which had been standing for two days over phosphorus pentoxide suffered only very slight combustion near the wires on discharge from the coil when at pressure of 700 mm., the mercury rising two millimetres in the tube, but no further action occurred. When a drop of water was introduced, the mixture exploded through the heat produced by the contact of the phosphorus pentoxide and water. Hence it was concluded that the greater the degree of dryness reached, the greater the pressure the gases can withstand without exploding under an electric spark. When the gases were sealed up with phosphorus pentoxide at just below atmospheric pressure, they did not explode on sparking. Even a pressure of 800 mm. could be attained in some cases without explosion. In a similar tube containing phosphorus pentoxide a piece of caustic potash was fused to the glass; on heating this gently with a Bunsen flame, the spark caused an explosion, the amount of moisture given up by the potash being apparently sufficient to determine the explosion.

Although a comparatively small number of water molecules sufficed to cause the reaction to proceed, the explosion gained in intensity the greater the number of water molecules present. It was shown by experiments at 52° C. that the force of the

¹ Beketoff, *Bull. Acad. St. Petersburg*, 2 (2), 175 (1891).

explosion was greater when the number of water molecules was equal to the number of carbon monoxide molecules than when fewer water molecules were present and their place taken by molecules of nitrogen of which the specific heat is less than half that of steam. The admixture of dry nitrogen was found to render a larger quantity of aqueous vapour necessary than when only carbon monoxide and oxygen were present.¹

Several other interesting experiments, all serving to impress the great importance of the moisture, were also described by Dixon. Thus if a *W*-shaped tube be used, with electrodes sealed through one end, the gas can be sparked as before without ignition, but if moisture be introduced to the end near the electrodes and the mixture be again sparked, the gas unites in the wet arm but not in the dry. Again, the flame of dry carbon monoxide burning in air may be extinguished by plunging it into dry air.² Even when carbon monoxide was passed through a platinum tube at a bright red heat, under which circumstances the flame turned a pinkish orange, the flame was still extinguished on plunging it into a jar of dry air quite as readily as without the heating. On withdrawing the tube from the jar, the gas immediately re-kindled on meeting the ordinary air.

In another series of experiments, Dixon³ compared the velocities of explosion of mixtures of carbon monoxide and oxygen with varying quantities of aqueous vapour by observing the pressure registered in a mercury gauge attached to the eudiometer. The results obtained are shown in Table I.

TABLE I.

	Tension of Carbon Monoxide and Oxygen.	Tension of Aqueous Vapour.	Reading of Pressure Gauge before Explosion.	Reading of Pressure Gauge after Explosion.	Pressure Registered in Gauge.	Temp. of Gases.	Length of Column.
	mm.	mm.			mm.	°C.	mm.
1	200	trace	229	236	562	33	500
2	"	trace	"	236·2	563	33·2	500
3	"	8·7	"	249·2	620	33	505
4	"	9·4	"	249·6	622	33·5	505
5	"	25	"	249·4	621	34	514
6	"	38	"	252·6	638	33·3	524
7	"	40	"	252·6	638	34	525

¹ *British Association Report*, 1882, p. 486; *Chem. News*, **46**, 151 (1882).

² *J. Chem. Soc.*, **69**, 774 (1896); cf. Traube, *Ber.*, **18**, 1890 (1885).

³ *British Association Report*, 1882, p. 487; *Chem. News*, **46**, 151 (1882).

In the first two experiments, only a trace of aqueous vapour was present. The eudiometer was dried at 80° C. in a current of dry air. In experiment 1, several sparks were passed before the mixture fired. In both experiments the flame took about two seconds to pass the 500 mm. along the tube. In the other experiments definite amounts of water vapour were added. Dixon suggested that the low results for the rate of explosion obtained by Berthelot and Vieille¹ were to be accounted for by their use of very dry gas.

Investigations were also made of the mean rate of explosion of carbon monoxide and oxygen through one metre with different quantities of water vapour present, the gases in each case being at atmospheric pressure. These furnished the results shown in Table II.

TABLE II.

Exploded at 10° C.		Exploded at 35° C.		Exploded at 60° C.	
Hygrometric State.	Rate in Metres per sec.	Hygrometric State.	Rate in Metres per sec.	Hygrometric State.	Rate in Metres per sec.
Dried by passing slowly over fresh P_2O_5	36	Dried by passing slowly over fresh P_2O_5	44	Dried by passing slowly over P_2O_5 used before	53
		Dried by passing slowly over P_2O_5 used before	69		
Dried by bubbling through 2 bottles of H_2SO_4	119	Dried by bubbling through 2 bottles of H_2SO_4	102	Dried by bubbling through 2 bottles of H_2SO_4	120
		Dried by bubbling through 2 bottles of H_2SO_4	103		
		Saturated at 6°	129		
		Saturated at 6°	123		
Saturated at 10°	175	Saturated at 8°	155	Saturated at 8°	158
Saturated at 10°	176	Saturated at 12°	200	Saturated at 8°	166
		Saturated at 35°	225	Saturated at 12°	211
		Saturated at 35°	226	Saturated at 35°	244
				Saturated at 50°	289
				Saturated at 60°	317

Other Early Investigations.—It was only natural that such results as those of Dixon should not pass without challenge.

¹ *Compt. rend.*, **95**, 151 (1882).

Indeed, it is very noticeable throughout the whole development of the study of the effects of intensive drying, both on chemical reactions and on physical properties, that each advance has been challenged, generally by investigators who have not realised at the time the intense degree of desiccation that is required to produce many of these effects, and the great precautions which have to be taken in order to attain it. Thus Botsch, working under the direction of Lothar Meyer, repeated some of Dixon's experiments and found that the mixture exploded "even when dried by phosphoric oxide."¹ On the other hand, he observed that reducing the pressure prevented the propagation of the explosion both in the wet and dry gases. Hence he suggested that Dixon's non-reactive gases were at a lower pressure than the moist specimens. Dixon's later, more detailed paper² explained this fully, however.

It was admitted later, by Meyer,³ that the negative results obtained by Botsch were due to inadequate drying. He found that a mixture of two volumes of carbon monoxide and one volume of oxygen which had been dried by contact with phosphorus pentoxide for six days over mercury in a eudiometer, and which was not ignited at 156 mm. pressure by a Ruhmkorff spark of low intensity, could be made to combine by passing through it a much more powerful spark continuously for two minutes, but combustion was not quite complete, and no explosion occurred. He suggested that this was due to equilibrium being attained between the dissociation of the carbon dioxide and the combination of the carbon monoxide and oxygen.

Traube⁴ and Beketoff⁵ also repeated many of Dixon's experiments.

The Dissociation of Carbon Dioxide.—It was first found by Dixon and Lowe⁶ that dry carbon dioxide dissociated to the extent of some 39 per cent. on sparking electrically, whilst this phenomenon was not observed with the moist gases. The equilibrium reached seemed to be the same as when carbon monoxide and oxygen were sparked together, for when 100 volumes of dry carbon dioxide were brought into one tube, and a mixture of 100 volumes of carbon monoxide and 50 volumes of oxygen into the other, and a series of sparks passed through both from the same coil, the volume of the carbon dioxide tube increased, and that of the carbon monoxide and oxygen tube

¹ *Ann.*, **210**, 207 (1882).

² *Phil. Trans.*, **175A**, 617 (1884).

³ *Ber.*, **19**, 1099 (1886).

⁴ *Ber.*, **18B**, 1890 (1885).

⁵ *Bull. Acad. St. Petersburg* (2), **2**, 175 (1891).

⁶ *J. Chem. Soc.*, **47**, 571 (1885).

diminished, till, after some hours, they became equal under the same pressure. On further passage of the spark, the two volumes fluctuated together as the nature of the spark varied, as shown in Table III.

TABLE III.

Time.	Corrected Volumes (c.c.).	
Hours	CO and O ₂	CO ₂
0	150.0	100.0
1	124.6	116.4
3	121.5	117.0
5	120.5	117.0
7	109.3	107.5
9	107.3	107.3
11	115.6	115.6
14	114.3	114.3

Treatment with a white-hot platinum wire caused no dissociation, so Dixon and Lowe considered that the carbon monoxide and oxygen reunited completely under the conditions of this experiment. Similarly, a mixture of dry carbon monoxide and dry oxygen combined completely under these conditions, although no flame was produced. This was doubtless due to the catalytic effect of the platinum wire, a phase of the problem which will be discussed later.

The Combination of Cyanogen and Oxygen. — Carbon monoxide has been shown to be an intermediate compound in the oxidation of cyanogen. Hence it is evident that the investigation of the influence of moisture on the combustion of cyanogen is interdependent on the investigations on carbon monoxide and oxygen. For this reason, it seems more convenient to deal with it here than to leave the subject to a later chapter.

The reaction between cyanogen and oxygen is of a special interest, since it is the most outstanding instance of a gas reaction which appears to be totally unaffected by the presence or absence of water vapour. This is very strange in view of the fact previously mentioned that carbon monoxide is an intermediate product of the combustion.

In his first experiments upon this system, Dixon¹ found that a mixture of one volume of cyanogen with ten volumes of air did not explode at any pressure from 100 to 800 mm. when it was electrically sparked in the dry state, but that on introduction of moisture it exploded at 305 mm., so it was concluded that moisture had a marked influence on the combination of these gases. Later, however,² he modified these views, since he found

¹ *Phil. Trans.*, **175A**, 617 (1884).

² *J. Chem. Soc.*, **49**, 384 (1886).

that the explosion of cyanogen and oxygen was, as far as he could tell, independent of the presence or absence of steam. The explosion depended purely on the nature of the spark, this accounting, presumably, for his former result. Exact measurements of the initial velocity of the explosion wave left little doubt that the addition of water vapour only impeded the reaction between the gases.

TABLE IV.

Hygrometric State.	Rate (Metres per Second).
P ₂ O ₅ dried	813
H ₂ SO ₄ dried	811
KOH dried	808
Saturated at 15° C.	752
Saturated at 15° C.	741

On heating a platinum wire to a white heat in a cyanogen-oxygen mixture, the gases combined silently, whether wet or dry. In the latter case, however, combination was not quite complete; of the cyanogen acted upon, about three-quarters was converted into carbon dioxide and the rest into carbon monoxide.

Confirmation of these results was obtained later, when Dixon, Strange, and Graham¹ found, contrary to expectations, that the flame produced by the explosion of a well-dried mixture of cyanogen with twice its volume of oxygen, when analysed photographically on a rapidly moving film, did not appear to differ from the flame given by the same gases mixed with 1.5 per cent. of water. Hence they concluded that "in a mixture of freshly formed carbon monoxide and oxygen, these gases unite as the mass cools down without the intervention of steam; and where steam is present it does not appreciably alter the time during which the change continues."

In this connection, some interesting results were obtained by Smithells and Dent² who succeeded in separating the cyanogen flame into two cones, an inner one of a peach blossom tint, corresponding to the oxidation to carbon monoxide, and an outer blue cone where the carbon monoxide burnt to carbon dioxide. They dried cyanogen by contact with phosphorus pentoxide, and then ignited the gas in a bottle of air dry enough to inhibit the combustion of carbon monoxide. The cyanogen flame, however, presented the usual appearance. A different result was obtained when the cyanogen was burnt in the cone separator and mixed with enough dry air to separate the cones widely. The outer cone was immediately extinguished when a bottle of dry air

¹ *J. Chem. Soc.*, **69**, 773 (1896).

² *Ibid.*, **65**, 603 (1894).

was brought over it. On approximating the cones again, a point was reached where the outer cone persisted. They concluded that when the carbon monoxide was hot its flame persisted in air dry enough to extinguish the flame of the unheated gas.

Even addition of dry cyanogen to a dry mixture of carbon monoxide and oxygen seems to be sufficient to cause its combination on sparking. According to Beketoff¹ the amount of cyanogen required for this purpose is 10 per cent., but probably combustion would be incomplete in this case, since Dixon² has found that with a mixture of 53·3 per cent. carbon monoxide, 6·7 per cent. cyanogen, and 40 per cent. oxygen, 32·3 per cent. of the initial carbon monoxide remained unburnt; whilst with 43·3 per cent. of carbon monoxide, 11·7 per cent. cyanogen, and 45 per cent. oxygen, 13 per cent. still escaped combustion. Carbon disulphide shows an exactly similar effect. From these facts Dixon concluded that it is possible to submit the dried mixture of carbon monoxide and oxygen to the intimate contact of a flame without causing complete combustion, but that the quantity of carbon monoxide burnt depends on the intensity of the exciting flame.

The Influence of the Nascent State on the Combination of Dry Carbon Monoxide and Oxygen.—Russell³ could find no evidence that the nascent state, *per se*, was very effective in causing the combination of dry carbon monoxide and oxygen. The state of affairs following on a violent reaction such as the explosion of carbonyl sulphide or of chlorine monoxide, had a very considerable influence in bringing about the combination of the carbon monoxide and oxygen, but whether this was a direct effect or due to a heightening of the action of the "third substance" he could not decide. When the conditions were made as nearly as possible the same, there seemed to be no great difference between the behaviour of nascent carbon monoxide and that of molecular carbon monoxide as studied by Dixon.

The interaction of oxygen and nascent carbon monoxide was first studied by an investigation of the explosion of carbonyl sulphide and oxygen. A mixture of these gases in the ratio 1 : 2 when sparked explodes violently, yielding carbon dioxide, sulphur dioxide, sulphur trioxide, and some sulphur. When the carbonyl sulphide was freed from hydrogen sulphide by standing for two or three days over mercuric oxide, and the mixture with

¹ *Bull. Acad. St. Petersburg* (2), **2**, 175 (1891).

² *J. Chem. Soc.*, **69**, 774 (1896).

³ *Ibid.*, **77**, 361 (1900).

oxygen dried for several days over phosphorus pentoxide, Russell found that an explosion still occurred on sparking, but much less violently and the combustion was incomplete. Even in the presence of an excess of oxygen, much sulphur was deposited and carbon monoxide remained unburnt. In fact, when the gas was transferred to another eudiometer, caustic potash added to absorb the products of combustion and any unchanged carbonyl sulphide, a residue of gas was left which exploded violently on sparking.

Analysis showed that of the original carbonyl sulphide, about 50 to 60 per cent. was burnt, 10 per cent. was unchanged, and 30 to 40 per cent. converted into carbon monoxide. When the carbonyl sulphide and oxygen were left for three weeks in contact with phosphorus pentoxide, less of the carbonyl sulphide was decomposed, 25 to 40 per cent. being burnt, 25 to 30 per cent. unchanged, and 30 to 40 per cent. converted into carbon monoxide. A small amount of carbon disulphide, however, caused more complete combustion. With 4 per cent. of this compound present, only 9 per cent. of carbon monoxide was found unburnt.

The reaction between nickel carbonyl and oxygen was also investigated for the same purpose. These two substances normally react vigorously in the cold, sometimes with violent explosion. Hence they were dried in a eudiometer with two chambers, so that they could be kept separate until dry. The nickel carbonyl was kept in a glass boat. After standing for a few days in contact with phosphorus pentoxide, the tap was turned so that the vapour of the carbonyl could diffuse into the oxygen. After an hour the tap was closed and the electrical spark passed, producing an explosion. Analysis showed that some carbon monoxide had escaped combustion, but not more than 3 per cent. These results were compared with those of Dixon, and were held to show that the greater the heat evolution of the reaction the more carbon monoxide was burnt. This was thought to be due possibly to the higher temperature to which the gaseous mixture was raised. It was also concluded that the nascent state of the carbon monoxide had no very great effect on the combustion.

The explosion of chlorine monoxide and carbon monoxide was tested in order to investigate the effect of the nascent state of the oxygen on the reaction with carbon monoxide. It was found that chlorine monoxide and carbon monoxide in the moist state combined almost completely in the dark in four to five days. Hence they were dried in separate bulbs connected by a tap for thirty hours at 0°C ., and then allowed to diffuse into one another

for an hour. An electrical spark was then passed. The gases left after absorption of chlorine were, carbon dioxide, 57 per cent.; oxygen, 39 per cent.; and carbon monoxide, 4 per cent. In a second experiment these figures were 60 per cent., 35 per cent., and 5 per cent. respectively. In each case about 6 to 7 per cent. of the carbon monoxide originally introduced was left unburnt, although the drying was far from complete and the explosion was vigorous.

Finally in order to have both the reacting gases in the nascent state, chlorine peroxide and carbonyl sulphide were dried together over phosphorus pentoxide for twenty-four hours in an ice chest, and were then exploded either by a spark or by heating in an air bath; the gases lost their deep green colour and became colourless. The amounts of carbon monoxide obtained under different conditions were as follows:—

With 1 volume carbonyl sulphide and $5\frac{1}{2}$ to 6 volumes chlorine peroxide—no carbon monoxide formed.

With 1 volume carbonyl sulphide and 4 to $4\frac{1}{2}$ volumes chlorine peroxide, $2\frac{1}{2}$ to 4 per cent. of the carbonyl sulphide was left as carbon monoxide.

With 1 volume carbonyl sulphide and less than $1\frac{1}{2}$ volumes chlorine peroxide, 20 per cent. was left as carbon monoxide.

Hence when carbon monoxide and oxygen, both nascent, are brought together and also heated by the flame of an explosion, combination is not complete.

Quantitative Investigations.—The first real attempt to test the effect of small, but known, amounts of water vapour on the explosion of a mixture of carbon monoxide and oxygen, was the little-known work of Girvan.¹ This investigator tested whether the drying of such a mixture by exposure to low temperatures, produced by either liquid air or solid carbon dioxide and alcohol, would be sufficient to prevent chemical action taking place when the gas was sparked after it had regained ordinary temperature. The apparatus was freed from moisture before the introduction of the prepared gas mixture by heating thoroughly in a current of dry air. Hence it was possible to estimate the amount of moisture left in the gas from the temperature of the freezing agent.

It was found that, whereas a series of powerful sparks from an induction coil would not ignite a mixture which had been dried at either -180° or -80° C., they would always do so

¹ *Proc. Chem. Soc.*, **19**, 236 (1903).

when the mixture had been dried at a temperature between -50° and -35° C., whilst a single spark would always cause an explosion if the drying had been at -15° C. only. He also remarked that "the explosion produced by powerful sparks in the gases dried between -50° and -35° C. is of a very different character from that obtained with the wet gases; the latter is very quick and violent, and gives a metallic click, but the former takes place quietly, and the explosive wave travels quite slowly along the tube."

Mixtures were also tested with the platinum terminals replaced by (a) a silver wire, and (b) a gold wire. Each was heated to redness and then fused by an electric current without visible action on an explosive mixture which had been dried at about -80° C. A platinum wire acted catalytically on the mixture (see p. 25).

Some calculations were also made of the amounts of moisture present in the mixtures after cooling, based on the following vapour pressure data:—¹

Temp.	$^{\circ}$ C.	-61	-56.5	-51	-45	-36
V.P.	mm.	0.008	0.01	0.029	0.052	0.160

Thus when the vapour pressure of the water was less than about 0.03 mm., as with the mixture after cooling to -50° C., the gases will not explode. When the partial pressure is less than about 0.16 mm. the explosion is very feeble.

Similar experiments have been carried out by Coehn and Tramm,² who found:—

(a) That a moist mixture could be exploded by a spark at any pressure.

(b) That a mixture dried by a short exposure to the action of solid carbon dioxide and alcohol cannot be exploded, but inflames and burns quietly.

(c) That a mixture which has been cooled for a sufficient time cannot be inflamed; a pale blue zone forms round the spark gap and slight combination occurs.

The Photochemical Reaction.—It was found by Chapman, Chadwick, and Ramsbottom³ that when a carbon monoxide and oxygen mixture was subjected to ultra-violet light, the presence of moisture increased the amount of carbon dioxide formed in a given time, but reduced the yield of ozone by a similar amount. Dry carbon dioxide was found to be decomposed under the

¹ *J. Chem. Soc.*, **49**, 46 (1886).

² *Ber.*, **54**, 1148 (1921).

³ *J. Chem. Soc.*, **91**, 942 (1907).

influence of ultra-violet light to the extent of 2.6 to 3 per cent. at atmospheric pressure, the oxygen being partially ozonised, whilst moist carbon dioxide was not at all dissociated. At 36 mm. pressure dried carbon dioxide was 46 per cent. dissociated, whereas the moist gas was still undissociated. These facts were explained by supposing the water to exert a marked influence on the mode of distribution of energy among the molecules of the reacting substances.

On the other hand, it was found by Thiele¹ that carbon monoxide and oxygen reacted in ultra-violet light as readily after careful drying as when in a moist condition. The same observation was made by Coehn and Tramm.² The latter observers dried a mixture of carbon monoxide and oxygen by means of liquid air till the partial pressure of water vapour was less than 0.004 mm., the mixture being then in such a state that it was non-explosive and at a high temperature reacted only slowly in the dark. When exposed to ultra-violet light, however, it exhibited the same velocity of reaction as a moist mixture.

The fact that dry carbon dioxide was decomposed by ultra-violet light, yielding an equilibrium mixture, was also confirmed by Coehn and Sieper.³ The presence of a very minute trace of water vapour greatly reduced the amount of decomposition; thus, whereas a dry gas under certain conditions of insolation was 18 per cent. decomposed, a trace of moisture reduced the amount of decomposition to 0.1 per cent. No trace of either formic acid or formaldehyde was produced, and the water remained entirely unchanged. They concluded that since it appears as though the presence of water vapour does not play a part in the union of carbon monoxide and oxygen under the influence of radiant energy, the reason of the markedly restrictive action of water vapour on the decomposition of carbon dioxide in ultra-violet light does not seem to be found in the inability of carbon monoxide and oxygen, once formed, to re-combine.

It appears that traces of other impurities can retard the photochemical decomposition of carbon dioxide, as well as water, e.g. potassium cyanide,⁴ and sulphur dioxide.⁵

The Reaction between Carbon Monoxide and Oxygen at a Catalytic Surface.—It was shown by Girvan⁶ that when

¹ *Ber.*, **40**, 4915 (1907); *Z. angew. Chem.*, **32**, 2478 (1909).

² *Ber.*, **54**, 1148 (1921); also Tramm, *Z. physikal. Chem.*, **105**, 356. (1923).

³ *Z. physikal. Chem.*, **91**, 347 (1916).

⁴ Peklo, *Bull. Boh. Acad.*, 1913, 100.

⁵ Tramm, *Z. physikal. Chem.*, **105**, 356 (1923).

⁶ *Proc. Chem. Soc.*, **19**, 236 (1903).

a mixture of carbon monoxide and oxygen had been dried by "freezing" at about -35°C ., a platinum wire acted catalytically, and in becoming heated to redness by an electric current caused a quiet and feeble explosion. When the mixture had been dried at between -80° and -180°C ., the platinum still acted catalytically, and glowed several seconds, but no other sign of reaction was observed. After glowing had ceased, the coil was maintained at a white heat for several minutes, and the gas then collected. About one-eighth of the mixture was carbon dioxide and the residue was still explosive, showing combination to be far from complete.

On the other hand, it was found that a gold or silver wire could be fused in a mixture dried at -80°C . without any visible action.

The influence of the presence of water vapour on the catalytic combustion of carbon monoxide and oxygen on surfaces of gold, silver, and porcelain, was thoroughly investigated by Bone,¹ It was found that the immediate effect of removing the moisture was to increase the apparent catalytic power of the surface, presumably by removing from it the film of water which normally lags it, more or less, according to its physical condition. The ultimate effect, usually observed only after prolonged drying, was to diminish greatly or to stop the catalytic combustion completely. With the two metal surfaces, the catalytic combustion was stopped completely, but on re-introduction of moisture the reactivity was in time restored. With porcelain, the ultimate effect was to diminish greatly the catalysing power, which, however, was not restored on re-introducing moisture.

The Influence of the Degree of Drying on the Minimum Spark Energy required for the Ignition of a Mixture of Carbon Monoxide and Oxygen.—It was shown by Bone and Weston² that progressive drying increased the minimum spark energy required to ignite a mixture of two volumes of carbon monoxide and one volume of oxygen at atmospheric pressure. Their results are summarised in Table V.

They showed that a mixture of two volumes of carbon monoxide and one volume of oxygen which had been dried to an extreme degree by six months' contact with pure phosphorus pentoxide could still be ignited and exploded, provided that a spark of sufficient energy be passed through it, although the gases displayed a much greater "resistance" to combustion than when even a minute amount of moisture was present. Whereas

¹ *Proc. Roy. Soc.*, **112A**, 474 (1926).

² *Ibid.*, **110A**, 615 (1926).

TABLE V.

Hygroscopic Condition of $2\text{CO} + \text{O}_2$ Mixture.	Saturated with Aqueous Vapour at $^{\circ}\text{C}$.	Per Cent. Water by Volume Present.	Minimum Igniting Capacity at 110 Volts, Mfds.	Energy of Minimum Igniting Spark $\Sigma = \frac{1}{2}cv^2$, Joules $\times 10^{-6}$.
Mixture "saturated" at room temp.	17.4	2.00	0.76	4,600
	17.0	1.98		
	14.5	1.70	0.83	5,020
	14.0	1.60	0.98	5,930
Mixture "saturated" at a low temp. controlled by ice or freezing mixture	4.0	0.80	4.00	24,200
	0.00	0.60	4.80	29,040
	— 5	0.40	8.00	48,400
	— 10	0.26	10.07	60,900
	— 16	0.16	17.25	104,350
Mixture calcium chloride- dried	— 25	0.06	18.79	113,800
	—	0.03	20.83	126,000

ignition could not be effected with a condenser capacity of 0.5 mfd. at 970 volts, i.e. with a spark energy of less than about 0.235 Joule, it always occurred instantly at about 0.77 mfd. or more, i.e. a spark energy of 0.362 Joule or more. The greater the energy, up to a limit, of the spark, the more complete the combustion. It varied from 74.3 per cent. at 0.362 Joule to 88 per cent. at 0.94 and at 2.35 Joule. The explosions were comparatively "soft" ones, no "click" being audible in any of them.

On this evidence, Bone and Weston suggested that there was some property of the electric spark, presumably its ionising power, which, if only developed strongly enough, can overcome the high resistance of such an extremely dry mixture to ignition and explosion, and by virtue of which it can, so to speak, compensate the system for the absence of water vapour.

The Influence of Pressure on the Explosibility of Dried Carbon Monoxide—Oxygen Mixtures.—According to Bone, Newitt, and Townend,¹ when the initial pressure is 50 atmospheres, the presence or otherwise of water vapour has very little influence on the rate of pressure development in the explosion of a mixture of two volumes of carbon monoxide with one of oxygen and four of nitrogen.

It was shown later by Bone, Fraser and Newitt² that the readiness of explosion of a mixture of carbon monoxide and

¹ *J. Chem. Soc.*, **123**, 2008 (1923).

² *Proc. Roy. Soc.*, **110A**, 634 (1926).

oxygen which had been dried over phosphorus pentoxide for twenty-two weeks, increased with increasing pressure. A spark gap of 0.01 inch was used. The results showed the following :—

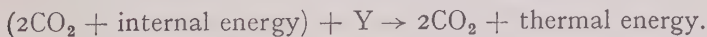
(a) At initial pressures below 2 atmospheres, none of the mixtures could be ignited by the sparking device used, no matter how many trials were made.

(b) At initial pressures of 2.75 to 5.0 atmospheres, the mixture could be ignited, usually only after several attempts, but combustion was never quite complete, 5 to 10 per cent. of the original carbon monoxide remaining unburnt.

(c) At initial pressures of 10 atmospheres or more, the mixtures were ignited instantaneously and at the first shot. Combustion was 99 per cent. and more complete.

Hence it would appear that it is only at pressures of less than about ten atmospheres that moisture has any effect on the explosion of these mixtures.

The Effect of Water Vapour on the Infra-Red Emission from the Flame and Explosion of Carbon Monoxide and Oxygen.—It has been shown by Garner and Johnson¹ that small traces of water vapour greatly depress the emission of infra-red radiation from the explosion of carbon monoxide and oxygen. This is accompanied by a corresponding increase in the rate of reaction. They consider that the reduction in intensity is due to collisions between water molecules and freshly formed molecules of carbon dioxide, i.e. with the emitters of 2.8 and 4.4 μ radiation. These molecules of carbon dioxide are supposed in the absence of water to give up their excess internal energy as infra-red radiation, but when water is present to lose this energy by collision. They suggested that the function of the water molecules is either to transform the internal energy of the activated molecules of carbon dioxide into kinetic energy directly, or as carriers of energy to molecules of carbon monoxide. According to either mechanism, some of the internal energy of the freshly-formed carbon dioxide, which is normally emitted as radiation, is retained in the gaseous system, and its retention serves to increase the rate of rise of temperature in the system. Thus the action of water and other positive catalysts, e.g. ethyl iodide and ethyl nitrate may be represented



They considered, however, that this did not rule out the possibility that ordinary catalytic effects may also be present.

¹ *Phil. Mag.* (iii.), **7**, 97 (1927).

The Influence of Traces of Other Gases.—An extremely interesting aspect of this subject is the observation of what other bodies can take the place of moisture in the promotion of chemical reaction. In the case of carbon monoxide and oxygen, the effect of several different other gases has been tested by Dixon and by Beketoff. The effects they have observed may be summarised as follows:—

(a) Traces of nitrogen,¹ nitrous oxide,^{1,4} carbon disulphide,¹ carbon dioxide,¹ sulphur dioxide,^{2,4} carbon tetrachloride² and nitrogen peroxide³ have no effect on the explosion of the dry mixture.

(b) One-eighth per cent. of dry hydrogen causes the mixture to burn slowly.¹

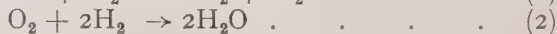
(c) A little ether causes explosion at 250 mm. pressure.¹

(d) Pentane,¹ hydrogen sulphide,¹ hydrogen chloride,¹ ethylene,² formic acid,² and ammonia² all cause combustion to proceed.

(e) Small quantities of cyanogen have no effect on the combination,¹ but the addition to the extent of 10 per cent. causes immediate explosion.⁴

From these observations, Dixon came to the conclusion that the property of conferring inflammability to a mixture was a general property of compounds containing hydrogen.

Theories of the Influence of Water Vapour on the Reaction between Carbon Monoxide and Oxygen. **Dixon's Theory.**—The mechanism originally suggested by Dixon to account for the intervention of water vapour in this reaction is that it takes place in two stages, as follows:—⁵



According to this view, it is the water which actually oxidises the carbon monoxide, the hydrogen produced reacting with oxygen re-forming water.

In support of this theory, Dixon pointed out⁶ that the only essential difference between the gases which determined the explosion of carbon monoxide and oxygen and those which do not, is that the former all contain hydrogen; thus,

Positive Instances, H_2O H_2S H_4C_2 H_2CO_2 H_3N H_{12}C_5 HCl .

Negative Instances, SO_2 CS_2 CO_2 N_2O C_2N_2 CCl_4 .

¹ Dixon, *Phil. Trans.*, **175A**, 617 (1884).

² Dixon, *J. Chem. Soc.*, **49**, 94 (1886).

³ *Ibid.*, **69**, 774 (1896).

⁴ Beketoff, *Bull. Acad. St. Petersburg* (2), **2**, 175 (1896).

⁵ *British Association Report*, 1880, p. 503.

⁶ *J. Chem. Soc.*, **49**, 94 (1886).

Hence he concluded that steam does not act as a mere third body, but in virtue of its own peculiar chemical properties. The following experimental observations also lent support to this theory :—

(a) When carbon monoxide was exploded with defect of oxygen in a moistened eudiometer, the carbon dioxide formed was more than twice the oxygen used, and a corresponding quantity of free hydrogen was found to be present in the residue.

(b) Hydrogen and oxygen appeared to explode under the action of an electric spark at exactly the same pressure wet and dry ; and a flame travelled at the same speed in each of the two gases, viz. at the speed of translation of steam molecules.

(c) Steam began to oxidise carbon monoxide at a dull red heat, and at a bright red heat about one-sixth was converted into carbon dioxide.

(d) On sparking a mixture of carbon monoxide and steam, carbon dioxide was formed, together with some formic acid.

(e) The reduction of carbon dioxide by hydrogen in presence of both resultant products was limited. Removal of one product, of course, pushed the reaction further.

However, as has been pointed out by Bone, several weighty objections can be levelled against Dixon's Theory :—

(a) The colour and general appearance of a carbon monoxide flame are very different from those of a hydrogen flame.

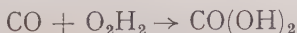
(b) A carbon monoxide flame radiates 2·4 times as much energy as a hydrogen flame of the same size.

(c) Such a very small quantity of moisture is required to produce the explosive reaction.

Traube's Hydrogen Peroxide Theory.—Another mechanism for the intervention of water in the oxidation of carbon monoxide was suggested by Traube.¹ Since he found that when electrical sparks were passed for some time through moist carbon monoxide, no carbon dioxide was formed, he supposed that carbon monoxide cannot decompose water at a red heat. Hence he suggested that the oxygen and carbon monoxide together acted on the water in the explosion, forming hydrogen peroxide and carbonic acid, thus,



and that the hydrogen peroxide then reacted with another molecule of carbon monoxide, thus,

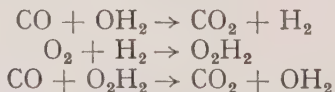


¹ *Ber.*, **18**, 1890 (1885).

the carbonic acid being, of course, immediately resolved into carbon dioxide and water. Traube actually showed that traces of hydrogen peroxide are formed during the combustion of carbon monoxide.

Dixon, however, pointed out¹ that since Traube had also shown hydrogen peroxide to be formed in the combustion of hydrogen and oxygen, the formation of the peroxide in the carbon monoxide flame might have been used as evidence that hydrogen combines with oxygen in the latter flame, and that, therefore, the steam had been decomposed by the carbon monoxide. Since Traube had come to a wrong conclusion concerning the possibility of the latter reaction, this course was not open to him. Dixon showed that in a cyanogen flame playing on to water, hydrogen peroxide was formed, as well as in the carbon monoxide and hydrogen flames, and that hydrogen peroxide was also produced on heating water in air. Hence the conclusion might be drawn that the formation of hydrogen peroxide was due to the heating of the water by the explosion or combustion.

Mendeléeff's Theory.—A modification of Traube's theory was suggested by Mendeléeff². He rejected Traube's first equation, considering that the carbon monoxide is oxidised directly by the steam, but he thought that the liberated hydrogen combines with a molecule of oxygen to form hydrogen peroxide, which in turn is reduced by more carbon monoxide :



This opinion was grounded on the conviction that gases enter into combination in equal volumes, and that the apparent exceptions to this law of nature are to be accounted for by supposing that such reactions are in reality complex, the initial reactions being between equal volumes. According to Mendeléeff, the law that reactions between equal volumes take precedence over all others afforded the simplest explanation for the necessity of the presence of steam to bring about the union of carbon monoxide and oxygen; since the direct oxidation of carbonic oxide by oxygen would involve an action between unequal volumes of gases.

This theory was attacked by Dixon³ on the grounds that

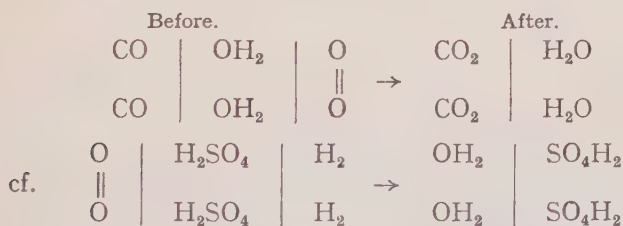
¹ *J. Chem. Soc.*, **49**, 94 (1886).

² *Principles of Chemistry* (English Edition), 1891.

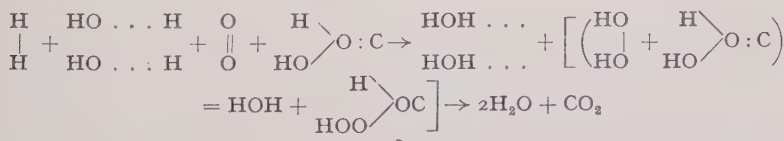
³ *J. Chem. Soc.*, **69**, 774 (1896).

reaction between carbon monoxide and nitrous oxide was also found to be stopped by intensive drying. Since the simple reaction in this case would be between equal volumes, Dixon contended that this explanation of the influence of moisture was insufficient.

Armstrong's Reversed Electrolysis Theory.—Yet another view of the rôle of water vapour in the promotion of the reaction between carbon monoxide and oxygen was put forward by Armstrong.¹ He likened chemical combination to a reversed process of electrolysis. Thus he compared the action of water in the combustion of carbon monoxide and oxygen to the action of sulphuric acid in Groves' gas batteries. He considered that to catalyse the carbon monoxide—oxygen reaction it was necessary for the catalyst to be divisible between the carbon monoxide and oxygen, and that this division must be into positive and negative radicles. The water was supposed to form a "closed conducting circuit" owing to the presence of some traces of electrolyte impurity. The oxygen was supposed to act as a depolariser, thus :



This view supposes that carbon monoxide and oxygen molecules are absolutely inert towards each other. Indeed, as recently as 1925,² Armstrong has declared that carbon monoxide is "*per se* an incombustible gas," adding that "an explanation may be found in the assumption that when a moist carbon monoxide mixture be sparked or fired, some hydrone is decomposed, and sufficient hydrogen set free to act in a 'depolarising circuit' together with the oxide," thus :



¹ *Proc. Roy. Soc.*, **40**, 288 (1884); *British Assoc. Presidential Address*, 1885; *J. Chem. Soc.*, **49**, 112 (1886).

² *Proc. Roy. Soc.*, **98B**, 202 (1925).

In opposition to Dixon, he supposes that the two reactions postulated by the latter occur simultaneously. He supposes it to be conceivable, however, that the action of the water may be of a "mechanical" order, that it may exert a mere contact action in bringing the carbon monoxide molecules and the oxygen molecules together.

It is not at all clear whether Armstrong considers that the water molecules are initially associated with either the carbon monoxide or the oxygen, but one rather gathers that it is supposed not to be so. In this case the reaction must be at least termolecular, or, from Armstrong's original equation, quinquemolecular, as has been pointed out by Dixon,¹ requiring the simultaneous collision of five molecules, two of carbon monoxide, two of water and one of oxygen. The chances in favour of such a collision are very remote. Dixon pointed out that, even if it did occur, heated steam and carbon dioxide molecules would fly in all directions, some colliding and reacting with unburnt carbon monoxide molecules, i.e. carbon dioxide would be formed in a manner independent of electrical conduction. Again, and this is perhaps the most serious drawback to Armstrong's hypothesis, it does not explain the oxidation of carbon monoxide in the combustion of cyanogen. Since neither nitrous oxide nor nitric oxide can replace water as a catalyst in the combustion of carbon monoxide, it cannot be supposed that oxides of nitrogen can replace water in Armstrong's "depolarising circuit."

Beketoff's Theory.—Beketoff² suggested that the function of moisture in assisting the combustion of a mixture of carbon monoxide and oxygen gases is that it acts by reason of the ready dissociation of its molecule into hydrogen and an atom of oxygen, which combines with the carbon monoxide. He pointed out that steam begins to dissociate at 800° C., whereas oxygen is stable at 2000° C. "The molecules of steam furnish the atomic oxygen which is indispensable for the combustion of carbonic oxide more readily than the molecules of oxygen themselves." The fact that 10 per cent. of cyanogen exerted an influence similar to that of water vapour he explained on the assumption that the heat liberated in the decomposition of the cyanogen is added to the heat of combustion of the carbon, with the result that the oxygen molecules themselves are broken up, causing the carbon monoxide to burn.

However, as was pointed out by Dixon³ this theory only puts

¹ *J. Chem. Soc.*, **69**, 774 (1896).

² *Bull. Acad. St. Petersburg* (2), **2**, 175 (1891).

³ *J. Chem. Soc.*, **69**, 783 (1896).

off the difficulty one stage. If carbon monoxide has not the power to break up the oxygen molecule, why should the liberated hydrogen be able to do so? The heat of formation of carbon dioxide is greater than the heat of formation of steam from hydrogen.

Wieland's Formic Acid Theory.—It was found by Wieland¹ that formic acid was one product of the hot combustion of carbon monoxide. He claimed that the formation of this compound as an intermediate step in the oxidation accounted for the necessity of water for the progress of this reaction, the combustion of the hydrogen of the acid being supposed to furnish the water necessary for the combination to proceed and to prevent the reverse reaction. This theory, he contended, was not in opposition to the views expressed by Armstrong. Wartenburg and Sieg² also supported the view that the reaction must be preceded by the formation of an unstable additive compound.

Tramm has shown, however,³ that mixtures of oxygen and formic acid cannot be exploded. Hence it does not appear to be possible that formic acid is the vital intermediate compound for this reaction.

Modern Views.—The view was first put forward by Lothar Meyer⁴ that the combination of carbon monoxide and oxygen can occur both directly and indirectly, but that a far higher temperature is required to initiate the interaction between carbon monoxide and oxygen than that between carbon monoxide and steam; so whereas the latter reaction is easily initiated by a spark of low intensity, the former requires one of high intensity.

Dixon⁵ criticised this theory on the grounds that not only was it difficult to understand how a flame of burning carbon monoxide and oxygen, which has a temperature estimated at 3000° C. at least, should be extinguished in the dried gases owing to the temperature not being high enough, whilst a red-hot platinum wire is admitted to be hot enough to bring about the combination, but that there was also the direct evidence of the extinction of the flame of heated carbon monoxide to show that the non-explosibility of a dry mixture of carbon monoxide and oxygen was not simply a result of insufficient temperature. Again it had been shown that complete combustion did not occur immediately on the explosion of cyanogen with excess of oxygen; on the contrary the extra oxygen appeared to be inert on the

¹ *Ber.*, **45**, 679 (1912).

³ *Z. physikal. Chem.*, **105**, 356 (1923).

⁵ *J. Chem. Soc.*, **69**, 774 (1896).

² *Ibid.*, **53**, 2192 (1920).

⁴ *Ber.*, **19**, 1099 (1886).

wave front, the carbon monoxide and oxygen combining only gradually behind the wave.

A good deal of evidence, however, has been obtained in recent years in support of Lothar Meyer's view, especially by Bone and his co-workers. Thus Weston,¹ who investigated the emission spectrum of the carbon monoxide flame, found that it consisted of two distinct parts, firstly a continuous and banded part, and secondly the "steam lines" in the ultra-violet region, characteristic of the hydrogen flame. Hence he came to the conclusion that in the flame of pure, but moist, carbon monoxide burning at atmospheric pressure in either air or oxygen, two sets of independent reactions occur simultaneously :—

- (a) Direct interaction between carbon monoxide and oxygen, exciting radiations which give rise to the continuous and banded part of the spectrum.
- (b) Interactions between carbon monoxide and water molecules which originate the "steam lines" of the spectrum.

Weston showed that in the spectrogram of a flame of sulphuric acid-dried carbon monoxide maintained in an atmosphere of sulphuric acid-dried oxygen, although the continuous and banded parts remain undiminished, the steam lines become exceedingly faint.

Similarly, Bone, Fraser, and Newitt² found that the spectrogram of the explosion at high pressure of a mixture of carbon monoxide and oxygen which had been dried over phosphorus pentoxide for twenty-two weeks showed no steam lines whatever. Hence they concluded that in this case the direct reaction took place without the intervention of moisture. Their results also indicated that increasingly high pressure favours the direct oxidation, so that with high initial pressures it predominated almost to the exclusion of the indirect oxidation.

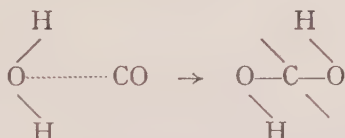
On the same grounds, Bone and Weston³ accounted for the fact that their carefully dried mixtures of two volumes of carbon monoxide and one of oxygen could be exploded, provided that a sufficiently powerful spark be employed. They suggested that there must be some property of the electric spark, presumably its ionising power, which, if only developed strongly enough, can overcome the high resistance of such an extremely dry mixture to ignition and explosion, and by virtue of which it can, so to speak, compensate the system for the absence of water vapour.

¹ *Proc. Roy. Soc.*, **109A**, 176, 523 (1925).

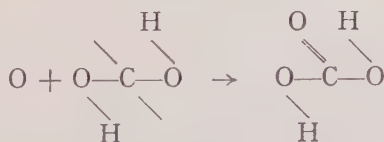
² *Ibid.*, **110A**, 634 (1926).

³ *Ibid.*, **110A**, 615 (1926)

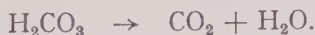
Similar views are held by Harrison and Baxter,¹ but they have developed a more elaborate view of the mechanism of the indirect oxidation through the medium of the water molecules. They consider that the action of the spark is to supply suitable radiation to the carbon monoxide molecules, driving some of the binuclear electrons into outer orbits—i.e. to activate the molecules—and that until a sufficient number of activated molecules are present combustion cannot be started. They suppose that molecules of carbon monoxide and water are probably associated in the gaseous state at ordinary temperatures, a carbon monoxide molecule tending to attract a water molecule into the co-ordination sphere, completely filling it and weakening the field between the carbon atom and the oxygen atom with which it is combined. When the gas is ignited, the binuclear electrons are driven into outer orbits. The oxygen of the water molecule readily captures one, causing a rearrangement in the carbon monoxide molecule, the valency of which now changes from a covalency to an electro-valency.



The dihydroxy compound produced will be extremely active and unsaturated, since the carbon atom has two free valency electrons. These will be shared with the nearest free oxygen atom, forming a molecule of carbonic acid :



At the temperature of the reaction this will be decomposed into one molecule of carbon dioxide and one of water,



It is not supposed that the molecule of water takes part in more than a few reactions; the carbon monoxide molecules which have no water associated with them are assumed to be oxidised directly. This is claimed to explain the quickening up of the

¹ *Phil. Mag.* (vii.), **3**, 31 (1927).

combustion and the greater ease of ignition in the presence of water vapour.

Summary.—As moisture is removed from a mixture of carbon monoxide and oxygen at ordinary pressures it becomes increasingly difficult to explode by means of an electric spark, but even after drying over phosphorus pentoxide for six months the mixture can still be exploded, provided a spark of sufficient energy be passed through it. The explosions in this case, however, are of a different character, taking place much more quietly and without the metallic click characteristic of the moist explosion.

A flame of dry carbon monoxide is extinguished on plunging into dry air.

The addition of steam increases the rapidity of inflammation of carbon monoxide and oxygen both in the ordinary flame and in the explosion wave.

It is only at comparatively low pressures that moisture appears to exert any influence on the combination of carbon monoxide and oxygen. Above ten atmospheres it appears to have no effect.

Other hydrogen-containing vapours appear to exert the same influence as moisture in determining this explosion, but traces of other gases appear to have no effect.

On continuous sparking of a dry mixture with a spark too small to cause explosion, dry carbon monoxide and oxygen combine slowly. The amount of the combination depends on the nature of the spark; a limit is reached when the rate of combination is equal to the rate of decomposition of the carbon dioxide formed.

The combination of cyanogen and oxygen appears to be totally uninfluenced by the removal of aqueous vapour, although carbon monoxide is an intermediate product in this reaction. The carbon monoxide proceeding from a half-burnt cyanogen flame will burn in dry air, providing that the two flames are sufficiently close together. However, the nascent state *per se* does not appear to be very effective in causing the combination of carbon monoxide and oxygen. When the dry gases are present whilst another violent reaction occurs, some combination takes place whether the reaction is such as to give one of the gases in a nascent form or not, but this is not complete.

In the absence of moisture, carbon dioxide is decomposed by ultra-violet light, yielding an equilibrium mixture. This does not occur in the presence of moisture or of certain other compounds such as potassium cyanide and sulphur dioxide. On the

other hand, dry carbon monoxide and oxygen insolated with ultra-violet light combine as readily as in the moist state, but presumably only up to the same equilibrium point as is reached with carbon dioxide.

The emission spectrum of the explosion of moist carbon monoxide and oxygen contains lines which are not present in the case of the dry gases.

The catalytic combustion of carbon monoxide and oxygen at surfaces is very much retarded or stopped completely on the removal of water vapour.

CHAPTER IV.

GASEOUS REACTIONS (*continued*).

THE SYSTEM HYDROGEN—CHLORINE—HYDROGEN CHLORIDE.

THE reaction between hydrogen and chlorine differs from that between carbon monoxide and oxygen in that a much higher degree of desiccation is required to retard its progress. Although the mechanism of this reaction, and particularly the manner in which water vapour determines its progress, is by no means clear, it may be taken as a typical example of a reaction upon the velocity of which an extremely minute trace of moisture can exert a very considerable influence. Further it has been much more completely investigated than any other reaction of this class. The matter is of supreme importance, since none of the suggested chain mechanisms can explain satisfactorily the manner in which hydrogen and chlorine combine until they can show in what stage of the reaction the water molecules exert their effect, and can also clear up the mysterious problem of how a few such molecules can influence the combination of a large number of others in a very brief period of time.

The Photochemical Reaction between Hydrogen and Chlorine.—The belief had already been expressed by Armstrong during his Presidential Address to the British Association in 1885,¹ that there would be no reaction between hydrogen and chlorine when these gases were pure and dry, but the first practical investigation was that of Pringsheim,² who described several interesting experiments on this subject. He found that if a dry mixture of hydrogen and chlorine were exposed to the feeble light of a petroleum lamp, the rate of combination was much less than in the case of a moist mixture under the same conditions. In the latter case combination was so rapid that a sulphuric acid index moved over 500 mm. in the first minute, whereas with the dry gases there was an induction period of a few minutes, and

¹ *British Association Report*, 1885, p. 963.

² *Ann. Phys. Chem.*, **32**, 384 (1887).

then a slow motion of the index set in, which, after a time, assumed the regular rate of 10 mm. per minute. Thus the reaction in this case was only one-fiftieth as rapid as in the former case. On shielding the dry bulb from the light, the movement was reduced to a millimetre in a few seconds, so it was concluded that the effect observed was not due to the slowness of the absorption of the hydrogen chloride. On the other hand, a bulb of the dried mixture brought into sunlight exploded with not perceptibly less violence than the moist mixture.

These results encouraged Pringsheim to try the effect of more careful drying still. With such gases, diffused daylight caused only a slow reaction or none at all, quite unlike the explosive results obtained with the moist gases under these conditions. In direct sunlight, there was an induction period of a second, and then fairly sudden combination occurred, with a faint flash of light and a faint crack. Only in very strong sunlight could a real explosion be brought about. The slow formation of hydrogen chloride in diffuse light was followed by the colour change due to the disappearance of the chlorine, the amount produced being afterwards determined by opening under water. The phenomena observed with the dry mixtures could all be repeated with the moist mixtures under less powerful illumination. Hence Pringsheim deduced that the phenomena in the case of the dry mixtures were essentially the same as with the moist.

In order to compare the action of light on the wet and dry mixtures of hydrogen and chlorine, Dixon and Harker¹ sealed up bulbs of the mixed gases, some in contact with phosphoric anhydride and the others without it. After lying in the dark for some weeks, a "wet" and a "dry" bulb, screened from one another, were exposed to the light of a standard magnesium "flash" placed some six feet from each. Neither exploded, but on firing such a flash five feet from the two, the "wet" bulb exploded loudly, whilst the "dry" bulb was unaffected. On firing at four and three feet from the "dry" bulb, no action was observed, but on firing at two feet the flash produced a loud explosion. When the gas was well dried before admission to the bulb, and was then sealed up with phosphorus pentoxide and kept for several weeks, the flash had to be brought within one foot to cause an explosion, i.e. the intensity of the light had to be increased twenty-five times in order to produce the same effect on the dry gases as on the moist mixture.

¹ *Manchester Literary and Philosophic Society Memoirs* (iv.), **3**, 118 (1889).

These observations were confirmed by Baker¹ who prepared a mixture of hydrogen and chlorine which did not explode on exposure to bright sunlight. The gases were dried in separate bulbs and mixed for twenty-four hours in the dark. Of this mixture only 75 per cent. combined after two days' exposure to diffused sunlight and two days in bright sunlight. Similar effects were noted by Gautier and Hélier² who found that when carefully dried hydrogen and chlorine in approximately equal volumes were exposed to diffused daylight in November for a day, the proportion of hydrogen chloride formed was only 2.55 per cent. as against 60 per cent. for a similar, but moist, gas mixture. In an hour in autumn sunlight, the percentages were 6.7 and 92.5 respectively. When exposed to albo-carbon lamps at a distance of a metre, combination occurred to the extent of 92.5 per cent. after 237 hours. The rate of formation of hydrogen chloride at first increased to a maximum of 2.8 per cent. per hour after three hours, and then decreased, but there seemed to be no limit to the extent to which combination would occur. In sunlight, the maximum rate of formation of hydrogen chloride was reached at a much earlier stage than in artificial light.

A more systematic study of this reaction was made by Mellor and Russell.³ They introduced pure chlorine and pure hydrogen into concentric bulbs, of which the inner and outer compartments were of approximately the same size. Redistilled phosphorus pentoxide was introduced into each. In the inner bulb was placed a sharp ended glass rod. Hydrogen was admitted to the outer bulb and chlorine to the inner. They were sealed off and left to dry in the dark for nine months. Immediately before an experiment, the bulbs were shaken in a dark place, so as to break the inner one, and a sufficient time allowed to elapse to ensure complete diffusion. It was then found that on exposing a bulb to bright sunlight in June, no explosion took place. After three days' exposure, the bulb was opened and the gas analysed. About 30 per cent. had combined.

Bevan⁴ found that the combination of dry hydrogen and chlorine gases under the action of light was much less rapid than when moisture was present, but that the general phenomena of induction were essentially the same, provided that sufficiently intense light be employed. There was a period of inertness and of acceleration. The rate of combination diminished as the gas

¹ *J. Chem. Soc.*, **65**, 611 (1894).

² *Compt. rend.*, **124**, 1267 (1897).

³ *J. Chem. Soc.*, **81**, 1272 (1902).

⁴ *Phil. Trans.*, **202A**, 71 (1903).

mixture was made less moist. In the case of a bulb containing phosphorus pentoxide as well as the gas mixture, combination was very slow, even in direct sunlight.

These results were denied by Bodenstein and Dux.¹ They found that the reaction velocity was unaltered when the partial pressure of water vapour was changed from 2.3 mm. to 0.004 mm. (i.e. when the chlorine had been dried by means of sulphuric acid and the hydrogen by slow passage first through sulphuric acid and then through a glass wool tube cooled to -78°C). Hence they concluded that perfectly dry chlorine and hydrogen may also combine in light at the normal rate, since it was possible that the experiments of the earlier workers had been vitiated by the circumstance that during the long period of drying with phosphorus pentoxide the gases had become so contaminated with inhibitors that interaction would not take place.

This view was criticised severely by Chapman² who urged that although small quantities of inhibitors are known to prevent the formation of hydrogen chloride under the influence of light, no known inhibitor can account for all the effects observed. It was also pointed out by Lewis and Rideal³ that in the so-called "dry" case in the experiments of Bodenstein and Dux, the reaction vessel was not baked out, and the chlorine contained a little oxygen, which undergoes photochemical hydrogenation with chlorine as the optical sensitising agent, so that the lower limit of the water vapour pressure may have been as high as 0.1 mm.

The matter was placed beyond all doubt by the work of Coehn and Tramm,⁴ who used still more careful methods of drying the gases. The gases were carefully purified and "moist" and "dry" mixtures were exposed in quartz tubes to the light of a 100 candle power Osram lamp. The gases were subsequently treated with neutralised potassium iodide solution, and the liberated iodine and hydrogen chloride were determined. Under such conditions, the union of hydrogen and chlorine in the presence of moisture occurred quantitatively in 12 minutes, whereas no sign of combination was observed in the dry tubes in two hours.

Quantitative measurements of a somewhat approximate nature were made by Coehn and Jung,⁵ who found that no union occurred on exposure to rays in the visible spectrum so long as the pressure of water vapour did not exceed 10^{-7} mm. of

¹ *Z. physikal. Chem.*, **85**, 297 (1913).

² *Trans. Faraday Soc.*, **21**, 548 (1926).

³ *J. Amer. Chem. Soc.*, **48**, 2553 (1926).

⁴ *Ber.*, **56**, 458 (1923).

⁵ *Ibid.*, p. 696; *Z. physikal. Chem.*, **110**, 705 (1924).

mercury. At a pressure of 10^{-5} mm., 88 per cent. was converted, whilst at 10^{-3} mm. maximum catalysis was reached. This data is extremely important in view of the fact already mentioned that very few measurements have been made of the actual quantities of water vapour required in order that the reactions may pursue their "normal" course.

On the other hand, it was found that a dry mixture, quite inert during exposure to daylight for twenty days or to illumination for forty minutes at 15 cm. distance from a 100 candle-power Osram lamp, was quantitatively converted into hydrogen chloride when exposed for twelve minutes at 20 cm. distance from a quartz mercury vapour lamp. A screen of "Uviol" glass, of which the transmission extends to 2540 Å. was sufficient to protect the mixture in a quartz tube from reaction. Hence the wave-length active in causing the combination of a dry hydrogen-chlorine mixture lies between 2200 and 2540 Å. The maximum wave-length producing the photochemical union of the moist gases was found to be 5400 Å.

The Thermal Reaction.—It was shown by Pringsheim¹ that a dry mixture of hydrogen and chlorine, which combined only slowly in the feeble light of a petroleum lamp, exploded violently on heating in a flame. A more carefully dried mixture exploded somewhat later, but just as violently as a moist mixture. Hence he concluded that the reaction in the case of the dry mixtures was essentially the same as in the case of the moist, differing only in degree, but that a greater light intensity or heating to a higher temperature was required to bring it about.

Using a similar method of drying to that employed in the case of their investigation of the photochemical union, Mellor and Russell² found that moist mixtures of hydrogen and chlorine combined at a much lower temperature than the gases which had been carefully dried. On simple heating, mixtures of the "moist" gases in similar bulbs exploded at 260° C. One bulb of the dry mixture was heated at 270° C. for some minutes but no explosion took place. The bulb was allowed to cool and the gases analysed. Very little combination could be detected. Another bulb was heated for ten minutes at 450° C. Still no explosion occurred, but analysis showed that about 80 per cent. of the mixture had combined. The phosphorus pentoxide in the tube had fused and some had volatilised.

¹ *Ann. Phys. Chem.*, **32**, 384 (1887).

² *J. Chem. Soc.*, **81**, 1272 (1902).

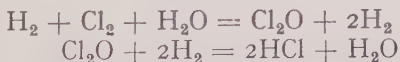
The Spark Reaction.—It was found by Dixon and Harker ¹ that sparks from an induction coil passed through a hydrogen-chlorine mixture between wires of platinum-iridium caused the instantaneous explosion of the mixture after it had been standing for some days in contact with phosphorus pentoxide. Hence the conclusion was drawn that the union of these gases was determined by the spark strength.

The same authors also studied the rate of propagation of the explosion wave in wet and dry mixtures of hydrogen and chlorine, ² finding that the mean velocity was 1795 metres per second in the "dry" tube and 1770 in the "moist" gases. Thus it seems that the explosion, once started, travels slightly faster in the dry gas mixture, the moisture appearing to act merely as a diluent.

Mellor and Russell ³ found that a small spark at once caused a violent explosion in dry hydrogen and chlorine, shattering the whole apparatus. The bulbs had been surrounded by a stout belljar, so that the amount of hydrogen left over could be estimated, but so little remained that it was concluded that combination had been complete.

The Dissociation of Hydrogen Chloride.—According to Coehn and Jung ⁴ dry hydrogen chloride does not dissociate under the influence of ultra-violet light.

Theories of the Influence of Water Vapour on the Reaction between Hydrogen and Chlorine. Intermediate Compound Theories.—In comparatively early days, Armstrong considered that the period of induction in this reaction was due to the time required for the formation of an intermediate compound, a reaction in which moisture was involved.⁵ Pringsheim ⁶ also concluded that an intermediate compound is formed. He thought it unreasonable to suppose this to consist of molecules of H_2Cl and Cl or of HCl_2 and H . Hence he sought the cause in the intervention of water. He assumed the reaction to occur in two stages, e.g.



He considered, however, that on heating vigorously or in bright light, the combination of the elements occurred directly.

¹ *Manchester Lit. and Phil. Soc. Memoirs* (iv.), **3**, 118 (1889).

² *Ibid.* (iv.), **4**, 3 (1890).

³ *J. Chem. Soc.*, **81**, 1272 (1902).

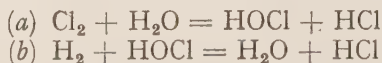
⁴ *Ber.*, **56**, 458 (1923).

⁵ *British Association Report*, 1895, p. 963.

⁶ *Ann. Phys. Chem.*, **32**, 384 (1887).

This theory was criticised by Mellor¹ on the ground that no obvious reason was offered why the chlorine monoxide formed is not absorbed by the water, the relative solubilities of chlorine monoxide and hydrogen chloride being very nearly in the ratio 5:1. Also he pointed out that Mellor and Anderson² had shown that a real period of inertness does not exist.

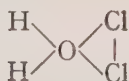
Veley modified Pringsheim's cycle³ and assumed the reaction to occur thus:



The reasons which he gave for this modification were, firstly that it is improbable that the anhydride Cl_2O would exist as such in the presence of water; and secondly that the researches of Pedler had shown that chlorine, in the presence of water and under the influence of sunlight, gives hypochlorous acid as an intermediate product. The view that hypochlorous acid was an intermediate compound in the union of hydrogen and chlorine was also favoured by Gautier and Hélier.⁴

This theory was also criticised by Mellor on the ground that it was not known whether hypochlorous acid vapour consists of $\text{H}_2\text{O} + \text{Cl}_2\text{O}$ or of HOCl . He also noted that the investigations of Pedler referred to by Veley applied to the action of light on aqueous solutions of chlorine.

B. Lewis⁵ suggested that a permanent chlorine hydrate



may be an intermediate compound in this reaction. This was based on the evidence he had obtained of the existence of such a compound in the case of bromine.

Molecular Complex Theories.—Mellor⁶ suggested that since chlorine acquires no appreciable chemical activity by exposure to sunlight, the presence of hydrogen as well as moisture must determine the greater activity of an induced mixture of hydrogen and chlorine gases. He supposed that if an intermediate compound takes part in the reaction between these gases in the presence of moisture the most probable "compound"

¹ *J. Chem. Soc.*, **81**, 1295 (1902).

² *Ibid.*, **81**, 414 (1902).

³ *Phil. Mag.* (v.) **37**, 170 (1894).

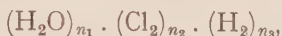
⁴ *Compt. rend.*, **124**, 1267 (1897).

⁵ *Trans. Faraday Soc.*, **21**, 584 (1926).

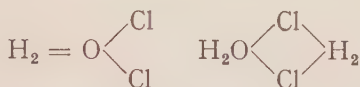
⁶ *J. Chem. Soc.*, **81**, 1292 (1902).

satisfying the required conditions contains $x\text{Cl}_2 \cdot y\text{H}_2\text{O} \cdot z\text{H}_2$, where x , y , and z are positive integers.

A similar theory was put forward, apparently independently, by Bevan,¹ who assumed that a complex was formed



from which molecules of hydrogen chloride afterwards split off. The induction period he assumed to be due to the time required for the formation of these intermediate compounds from water vapour and the two gases. He considered it probable that the chlorine and water combined first, the hydrogen then adding on, thus:



and that this finally breaks down into water and hydrogen chloride.

In more recent years, Weigert² has put forward the view that an "adsorption complex" of $\text{H}_2\text{—Cl}_2\text{—H}_2\text{O}$ is necessary for the primary process before the chain sets in, and that the presence of the water vapour enables a smaller quantum to start the reaction than would otherwise be the case.

Marshall³ supposed that the quantum absorbed by chlorine from visible light may be insufficient to cause it to react with hydrogen, and that it may receive some of its energy of activation from the polar water molecules present in the gas, and that it is a molecular complex of water and chlorine which initiates the primary reaction with hydrogen.

Chain Mechanisms Involving Moisture.—A mechanism by which water vapour may enter the "Nernst Chain" in the combination of hydrogen and chlorine has been suggested by Stern and Volmer.⁴ They took the view that collision is necessary before an active molecule can break up, and suggested that the first stage in the reaction may be



followed by the reaction



etc., as in the Nernst chain.

¹ *Phil. Trans.*, **202A**, 71 (1903).

² *Z. physikal. Chem.*, **106**, 407 (1923).

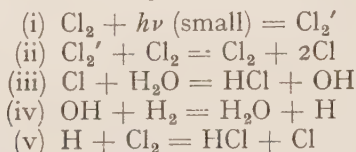
³ *J. Physical Chem.*, **29**, 842 (1925).

⁴ *Z. wiss. Photochem.*, **19**, 275 (1920).

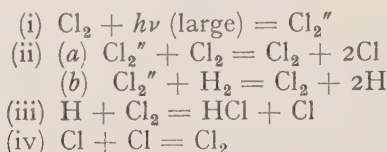
According to this mechanism, the velocity of reaction would be independent within wide limits of the water vapour concentration, as has been found by Bodenstein and Dux.

Coehn and Jung¹ suggested two different mechanisms for the wet and dry mixtures respectively, the former involving a chain mechanism but the latter none:—

A. Wet—in visible light:



B. Dry—in ultra-violet light:



Coehn and Jung assume the impossibility of the probably endothermic reaction $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ in the mechanism suggested by Stern and Volmer.

Weigert² has criticised Coehn and Jung's theory as involving water in the chain, in which case the water vapour concentration would be of importance. Again Cathala has pointed out³ that the relative number of impacts which would take place between chlorine atoms and water molecules on the one hand, and between two chlorine atoms on the other hand in Coehn and Jung's experiments in no way corresponds with the numbers necessitated by the high quantum efficiency obtained. If every contact between chlorine atoms and water molecules is fruitful, then only one out of every 26,000 collisions between chlorine atoms results in recombination. If only a fraction of the former collisions are fruitful then the figure is higher still. This Cathala holds to be untenable.

In a critical survey of the subject⁴ Lewis and Rideal came to the conclusion that it was improbable that water actually enters into the chain mechanism, though at the same time they considered that Weigert's objections to Coehn and Jung's mechanism from the quantitative stand-point are inconclusive.

¹ *Ber.*, **56**, 696 (1923); *Z. physikal. Chem.*, **110**, 705 (1924).

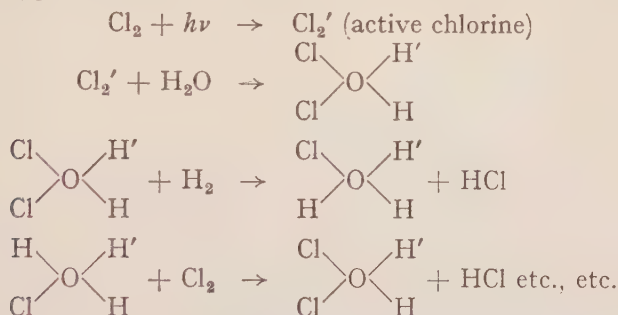
² *Ibid.*, **106**, 407 (1923).

³ *Compt. rend.*, **181**, 33 (1925).

⁴ *J. Amer. Chem. Soc.*, **48**, 2553 (1926).

Assuming the Nernst chain, Bowen¹ suggests that water acts by virtue of a surface action on the walls of the vessel, preventing the union of hydrogen atoms to molecular hydrogen, a reaction which would end the chain.

Chapman² proposed a chain mechanism of a new, addition product, type:—



This theory was severely criticised by Weigert³ who pointed out that Weigert and Kellermann's experiments, as well as those of Bodenstein and Dux indicated that water was involved in the primary process and not in the following chain.

Yet another type of chain mechanism has been suggested recently by Rollefson.⁴ From experiments on the rate of photochemical reaction between hydrogen and chlorine at low pressures, it was concluded that the chlorine molecule must be dissociated by light into a normal atom and one in a $^2\text{P}_1$ state. Water can have no effect on this process, since it has been shown that moist and dry chlorine have identical absorption spectra (see p. 132). The possibility of an addition product with water which has too small an absorption to be noted is rejected because it is considered that the concentration of such a complex, and hence the rate of reaction, should be dependent on the water vapour pressure up to a higher pressure than that found experimentally, viz. 10^{-5} mm. Hence he concludes that one or both atoms formed by the action of the light must react with water to start the chain process, and of such reactions he favours the formation of an addition product $\text{Cl} \cdot \text{H}_2\text{O}$, since any other reaction such as $\text{Cl} + \text{H}_2\text{O} = \text{HCl} + \text{OH}$ might be expected to be followed by reactions in which oxygen might be formed, and there is no indication of this. If it were the normal atom which reacted, the

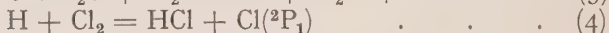
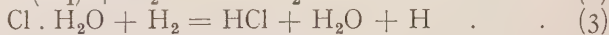
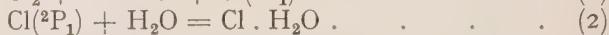
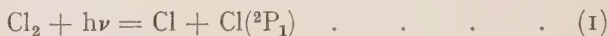
¹ *J. Chem. Soc.*, **125**, 1233 (1924).

² *Trans. Faraday Soc.*, **21**, 545 (1926).

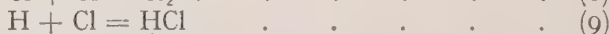
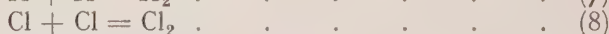
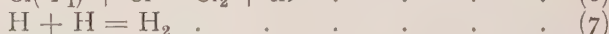
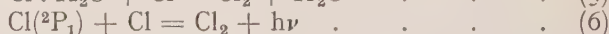
⁴ *J. Amer. Chem. Soc.*, **51**, 770 (1929).

³ *Ibid.*, 583 (1926).

rate should depend on the relative number of water molecules and chlorine atoms, which means that under a given set of conditions the rate should be approximately linearly proportional to the water-vapour pressure. On the other hand, if it is the activated chlorine which reacts, the number of atoms remaining in the active state long enough to react with a water molecule falls off exponentially as the water-vapour pressure is decreased. This is in accord with the experiments of Coehn and Jung. Using their data, Rollefson calculates the life period of the metastable state of chlorine to be about a fiftieth of a second, which he considers to be a reasonable value. Starting in this way he builds up the following series of reactions:—



The chain may be terminated by such reactions as



With low pressures of hydrogen, the limiting reactions will be (5), (6), and (8), but with low chlorine concentrations reaction (7) will play an important part. This theory is claimed to agree with experiments on the rate of photochemical reaction between these two elements.

Activation Theories.—It was suggested by Cathala¹ that the water molecule as an electric dipole and by virtue of its stray force field, must materially influence the structure of the potentially reactant molecules in its vicinity in the direction of greater reactivity. He also postulated that the radius of the sphere of activity of a water molecule varies directly with the intensity of the light, and that while at low pressures the catalytic activity is proportional to the pressure of the water vapour, it rapidly reaches a maximum as the concentration is increased. The point at which the maximum is attained is, presumably, that at which the volume of the combined spheres of action just equals the total volume of the reaction vessel.

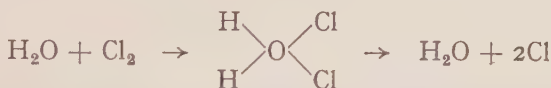
This was criticised by Norrish² who calculated from Coehn and

¹ *Compt. rend.*, **181**, 33 (1925).

² *Trans. Faraday Soc.*, **21**, 575 (1926).

Jung's data that according to this theory the radius of the sphere of action of the water molecule for light of the intensity used by them must be about 10^{-4} cms., a value which seemed to be extremely high compared with molecular dimensions. He also pointed out that it is not at all obvious why the catalytic activity should not increase even after the combined volumes of the spheres of action just fill the reaction vessel.

Norrish¹ assumed that the primary photochemical reaction—the dissociation of the chlorine molecules into atoms—requires water as a catalyst, and takes place only at the water film covering the walls of the vessel. He supposed the initial reaction between chlorine and water to occur as follows :—



The velocity of activation is supposed to be uninfluenced whilst the surface layer of water is saturated, but to decrease at low water vapour pressures where the surface layer is incomplete. He calculated that in Coehn and Jung's apparatus the monomolecular film was just complete at a water vapour pressure of 10^{-3} to 10^{-4} mm. The water-chlorine complex, being formed only on the surface of the vessel, is considered to be so structurally weakened by adsorption that light can bring about its decomposition into water molecules and chlorine atoms, the Nernst chain then following. He contended that these Nernst chains must extend outwards into the gaseous phase and be destroyed on again meeting the surface. This theory leads to an expression which Norrish considers to be in full agreement with Chapman's experiments on the reaction between moist hydrogen and chlorine.

As pointed out by Weigert, however,² it has been shown that the reaction takes place exactly in the beam of rays entering the vessel.³ If the primary photochemical reaction took place at the surface of the wall, the chain inside the vessel would be a simple dark reaction, and exact coincidence of the Töpler stria with the geometrical form of the beam could not be true. Again, it has been shown by Coehn and Heymer⁴ that hydrogen chloride is formed on exposing a mixture of hydrogen and chlorine to the action of visible light without contact with a solid surface.

¹ *J. Chem. Soc.*, **127**, 2316 (1925), and *loc. cit.*

² *Trans. Faraday Soc.*, **21**, 583 (1926).

³ Weigert and Kellermann, *Z. physikal. Chem.*, **107**, 1 (1923).

⁴ *Ber.*, **59B**, 1794 (1926).

Hence the reaction cannot depend on the initial catalysis of the glass wall.

Summary.—Hydrogen and chlorine do not combine in visible light so long as the partial pressure of water vapour present does not exceed 10^{-7} mm. At 10^{-5} mm. some combination occurs, and at 10^{-3} mm. maximum catalysis is reached.

Mixtures too dry to react at any observable rate in visible light combine readily in ultra-violet light. The wave-length producing this combination lies between 2200 and 2540 Å. A mixture has not yet been prepared which is too dry to react under these conditions.

A dry mixture does not explode on heating even to temperatures much above the usual explosion point, but in the only series of experiments so far recorded, slow combination took place.

Dry hydrogen chloride does not dissociate under the influence of ultra-violet light.

CHAPTER V.

GASEOUS REACTIONS (*continued*).

THE UNION OF HYDROGEN AND OXYGEN.

OF the many reactions which are influenced by the presence of water vapour, probably the most interesting is that between hydrogen and oxygen, in which water is produced. Thus if only a very little moisture is allowed to remain in the system, the reaction should be very markedly autocatalytic. Hence it is only to be expected that very thorough drying indeed will be required in order to produce any observable effect on this reaction. This, indeed, appears to be the case, as the experiments described below have shown.

The Spark Reaction.—In the first work on this subject recorded, Dixon,¹ as a result of several careful experiments, came to the conclusion that equal volumes of air and electrolytic gas exploded equally well whether moist or dried over phosphorus pentoxide. He started at low pressures and increased the latter by 5 mm. at a time. In both cases the gases did not explode at 70 mm. pressure, but did so at 75 mm. Hence Dixon came to the conclusion that the reaction between hydrogen and oxygen was unaffected by the presence or absence of water vapour.

As, however, was soon pointed out by Traube² the case was by no means proved. Even allowing that the drying had been adequate, Dixon had used platinum conducting wires, and this metal is known to cause the union of hydrogen and oxygen even at ordinary temperatures. This, indeed, is the great difficulty in investigating the spark reaction between these two elements. Complex as is a spark reaction of any type, it is here further complicated by the fact that almost any element of which the electrodes can be made acts as a contact catalyst between the two gases at the temperatures attained during the sparking, if not even at ordinary temperatures. The effect of

¹ *Phil. Trans.*, **175A**, 617 (1884).

² *Ber.*, **18B**, 1894 (1885).

moisture on the catalytic combination of these two elements will be dealt with later.

A much more careful drying technique than that of Dixon was employed by Baker,¹ but still the same result was obtained, for out of twenty experiments carried out to test whether electric sparks could be passed in the dried gas without explosion, only in one case was this successful, and this only with extremely small sparks.

The Thermal Reaction.—The thermal combination of hydrogen and oxygen was also studied by Baker,² who was able

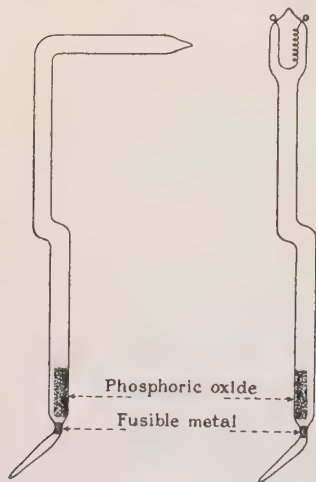


FIG. 1.

FIG. 2.

to show that this reaction can be considerably inhibited and even stopped completely on very careful desiccation. Tubes of either Jena or hard Bohemian glass were bent into the shape shown in Fig. 1. These were cleaned and washed, and then heated to redness whilst a current of dry air was drawn through them. A plug of redistilled phosphorus pentoxide was introduced, the upper end of the tube drawn off, and the lower end drawn out to a capillary of about 0.5 mm. diameter. A small piece of fusible metal was introduced, and the tube was exhausted. It was then connected with an electrolysis apparatus, the mixed gases being

dried roughly by passing them through a phosphorus pentoxide tube a foot long. The barium hydroxide used in the electrolysis apparatus had been recrystallised fifteen times. When the tube was nearly full of gas, the fusible metal was melted and allowed to run into the capillary. The other portion of the capillary was then sealed off. The tubes were allowed to stand in the dark for varying periods. Comparison tubes were made at the same time from the same length of tubing, and treated in precisely the same way, except that no phosphorus pentoxide was sealed up in them.

After ten days' drying, a pair of such tubes were heated side by side in the same Bunsen flame. In twelve experiments the "wet" tube exploded and the "dry" tube did not. In one

¹ *J. Chem. Soc.*, **81**, 400 (1902).

² *Loc. cit.*

experiment only did a dry tube explode, and in that case it was probable that some of the phosphorus pentoxide had been shaken into the part of the tube that was heated. Each of the twelve tubes which had been heated without explosion were opened under dry mercury; a very small contraction was observed in some tubes, but in most of them none at all. On addition of a small quantity of distilled water, the contents of each tube exploded on bringing them to a flame. A most extraordinary phenomenon was observed in two experiments where only two days' drying had been allowed. Water was slowly formed in the dried tube, but even when visible moisture was present on the walls of the tube, no explosive combination took place, and slow combustion only occurred.

In order to see whether increasing the temperature beyond the ordinary temperature of explosion produced any effect, a thin coil of silver was attached to platinum wires by fusion, and the latter sealed through the walls of a hard glass tube (Fig. 2). The tube was dried as before and filled with the explosive mixture. It was found that no explosion took place when the silver was heated to its melting-point by an electric current. No contraction was observed on opening the tube under mercury.

Baker explained the non-reactivity of the dried gases by supposing that union can only take place through the ions produced by the dissociation of the gases. This was supported by the observation that a feeble electric discharge would not pass through the gas when carefully dried. He also assumed on Armstrong's Theory that the water formed by the union of the very pure gases is itself very pure, and so cannot act as an electrolyte in causing the explosion of the gases.

On standing over phosphorus pentoxide in the dark, the electrolytic gas mixture showed no volume change, even after six months.

Some interesting experiments on this subject have also been carried out by Bone and Andrew.¹ After drying a mixture of pure electrolytic gas for four weeks, they found that there was an enormous difference in the rate of combination in the moist and dried gases during ten minutes at 525° C., the amounts of combination observed in the undried gas being 52, 45, 42, and 40 per cent. respectively, and in the dried gas 0.5, 3.0, nil, and 3.0 per cent.

Baker's experiments were repeated by Dixon and Edgar.² After drying a very pure electrolytic gas mixture for forty days,

¹ *J. Chem. Soc.*, **89**, 652 (1906).

² Dixon, *J. Chem. Soc.*, **97**, 661 (1910).

they heated a silver wire in the gas. They came to the conclusion that a higher temperature was required to start the reaction in the dried gas than in the moist, but that combustion occurred in both cases, and drops of water condensed on the cool part of the tube. Explosion could be brought about, however, at a sufficiently high temperature. From these experiments, Dixon came to the conclusion that water must intervene in the initial action of hydrogen and oxygen, but he did not consider it necessary for the propagation of a flame once started.

Baker's work was also repeated by Coehn and Tramm¹ who confirmed the observation that mixtures of hydrogen and oxygen which had been desiccated by drying for three weeks in contact with phosphorus pentoxide could be heated to redness in Jena glass tubes without the occurrence of an explosion, slow combination only occurring.

The Photochemical Reaction.—In the course of his earlier series of experiments,² it was shown by Baker that when a tube of dried hydrogen-oxygen mixture was exposed to sunlight for four months, it showed no change in volume, whilst an undried mixture showed a contraction of one twenty-third of its volume in the same period of time.

On the other hand, Coehn and Tramm³ found that drying the explosive mixture for three weeks did not appear to exert any appreciable influence on the rate of combination of the two gases when exposed to the ultra-violet light of the Heraeus lamp.

The degree of desiccation attained by Coehn and Tramm, however, cannot have been so great as that which was reached a little later by Baker and Miss Carlton,⁴ who found that the photochemical reaction in ultra-violet light could be very considerably retarded and even stopped completely by drying. As in the previous experiments, the gaseous mixture was obtained by electrolysis of very pure barium hydroxide. The reaction tubes were of clear fused quartz, bent into an *L* shape, the shorter arm being closed. The tubes were dried carefully, and filled with very pure dry mercury, and the electrolytic mixture introduced over the mercury trough. Pairs of tubes of equal size were made, one containing phosphorus pentoxide and the other none, and they were left in the dark for the specified time.

Pairs of tubes were then arranged near a quartz mercury vapour lamp, so as to be exposed as nearly as possible to the same radiation. The parts of the tube containing the phosphorus pentoxide were shielded from the direct rays of the lamp. The

¹ *Ber.*, **56B**, 455 (1923).

² *Loc. cit.*

³ *Loc. cit.*

⁴ *J. Chem. Soc.*, **127**, 1990 (1925).

extent of the reaction was deduced from the rise in the mercury column. The results which were obtained are given in Table VI.

TABLE VI.

	Period of Drying.	Time of Exposure to Light, hrs.	Rise in Mercury Column.	
			"Dry," mm.	"Wet," mm.
1	2 weeks	7	4	14
2	3 weeks	5	4	30
	after 12 hours interval	6	9	42
3	4 weeks	5	0	6.1
	after 12 hours interval	3	1	4.5
	after 12 hours interval	5	6.5	7.2
4	7 weeks	6½	0	2.3
	after 12 hours interval	6½	0.35	6.5
5	8 weeks	5	0.5	5
	after 12 hours interval	5	0.1	5
6	10 weeks	5	0	6.1
	after 12 hours interval	6	0	6.2
	after 12 hours interval	9	0.5	9.1
	after 12 hours interval	8½	1.5	10
	after 12 hours interval	6	10	12.5
7	18 weeks	13	0	—

It was presumed that during the twelve-hour intervals renewed drying occurred, so that only a fraction of the water produced one day was available for promoting chemical reaction on the next. In experiments 3 and 6, however, there was a sudden rise in the extent of the reaction, the amount of water formed being too much to be absorbed during the night. No mercury "tailing" was observed, showing that no ozone was formed.

The Catalytic Reaction.—It was first discovered by French¹ that dry spongy platinum does not catalyse the combination of a dry mixture of hydrogen and oxygen.

Baker² found that a coil of thin platinum wire suspended in a mixture of hydrogen and oxygen seemed to have no catalytic effect on the explosive mixture even when the latter was only imperfectly dried. After sealing with phosphorus pentoxide for ten days, there was no appearance of moisture on the surface of the pentoxide. As this is a fairly sensitive test for the presence of water vapour, it was concluded that no appreciable combination had occurred. The temperature of the platinum coil was raised gradually, and just after reaching visible redness, the mixture exploded. On the other hand, a silver wire could be heated

¹ *Chem. News*, **81**, 292 (1900); *Proc. Chem. Soc.*, **175**, 52 (1897).

² *J. Chem. Soc.*, **81**, 400 (1902).

to fusion in the mixture without explosion occurring. Hence the catalytic activity of the platinum was apparently sufficient to bring about the union of the dried and purified gases at a dull red heat.

In discussing this problem it may also be mentioned that it was discovered by Traube¹ that moisture plays a part in the oxidation of the so-called palladium hydride, produced by adsorbing hydrogen in palladium. Normally the hydride exhibits the property of spontaneous oxidation in air at ordinary temperatures, the metal becoming red hot; but Traube found that a piece of palladium foil charged with hydrogen could be left in a vessel containing air over sulphuric acid for two days without any change in volume of the air taking place. Hence he came to the conclusion that the oxidation of palladium hydride occurred through the medium of water. Similar results were obtained when the gas was confined over a syrupy solution of phosphoric acid containing excess of phosphorus pentoxide, but, when the solution was diluted with water, reaction occurred.

Summary.—Our present knowledge of the influence of moisture on the combination of hydrogen and oxygen may be summarised as follows.

Pure hydrogen and oxygen can be heated to the melting-point of silver without combination after drying with phosphorus pentoxide. If only partly dried, the gases unite slowly on heating, and although visible water formed in this way may be present, no explosion occurs.

The undried gases unite slowly in sunlight at ordinary temperatures, but the dried gases do not. Gases dried to such an extent that they will not combine in visible light may still do so in ultra-violet light. If very careful desiccation is carried out, however, the reaction in ultra-violet light also ceases.

A mixture of hydrogen and oxygen seems to combine under the influence of an electric spark even after drying very carefully.

Dry platinum does not appear to catalyse the reaction between dry hydrogen and dry oxygen at room temperature, but it seems to be able to catalyse the combination at a dull red heat.

¹ *Ber.*, 18B, 1877 (1885).

CHAPTER VI.

GASEOUS REACTIONS (*continued*).

THE SYSTEM NITRIC OXIDE—OXYGEN—NITROGEN PEROXIDE.

As long ago as 1884, Armstrong predicted that there would be no reaction between nitric oxide and oxygen gases if they were intensively dried before being mixed.¹ The first experimental attempt to carry this out, however, was quite unsuccessful, as Emich found² that these gases reacted even after careful preliminary drying with alkali or with phosphorus pentoxide. This Emich considered to disprove Traube's hypothesis³ that no substance will react with oxygen at ordinary temperatures without the intervention of water.

Baker's Investigation.—The problem was much more closely investigated by Baker, who showed⁴ that nitric oxide prepared by the action of nitric acid on copper seemed to react with oxygen as well dry as moist. The effect was different, however, with the gas prepared by warming the black compound of nitric oxide and ferrous sulphate. The gas so evolved was washed by passage through several long tubes containing water, and dried with sulphuric acid. It was introduced into one half of a tube divided in the middle by a tap, the whole of which had previously been exhausted. Pure oxygen was admitted to the other half of the tube. Each part of the tube contained plugs of phosphorus pentoxide, which dried the gases separately. After ten days, the tap was opened and the gases allowed to mix, but no darkening of the gas could be seen, and on opening under mercury, no contraction in volume was observed. When a small quantity of water was introduced, dense brown fumes of nitrogen tetroxide were formed.

Influence of the Nature of the Walls of the Containing Vessel on the Combination of Nitric Oxide and Oxygen.—The velocity constant of the reaction between nitric oxide and

¹ *Proc. Roy. Soc.*, **40**, 288 (1884).

² *Monatsh.*, **13**, 86 (1892).

³ *Ber.*, **18**, 1881 (1885).

⁴ *J. Chem. Soc.*, **65**, 611 (1894).

oxygen under varying conditions has been determined by Hasche.¹ His results are summarised in Table VII.

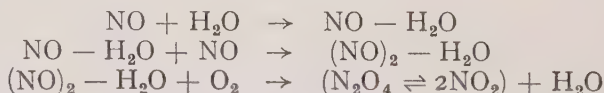
TABLE VII.

Expt.	Conditions of Expt.	Evacuated to	Speed at Zero Time.	Initial Pressure.		Induction Period.	Average Velocity Constant, $\times 10^{-7}$.	Average Deviation.
				O ₂ mm.	NO mm.			
25	Glass	$10^{-4}(a)$	1	105.2	74.1	present	4.69	0.08
2	Glass	$10^{-4}(a)$	10	172.5	183.0	none	4.69	0.11
7	Paraffin	$10^{-4}(a)$	4	142.7	128.0	present	3.58	0.21
27	SO ₂ in glass	$10^{-4}(a)$	2.6	102.3	122.3	present	4.44	0.08
36	N ₂ O ₄ in glass	$10^{-4}(a)$	1.9	98.7	105.0	present	4.93	0.19
26	Water for 48 hours	$10^{-4}(a)$	1.7	115.5	91.0	none	5.16	0.06
20	Glass in equilibrium with air	10^{-3}	1	78.1	86.2	present	5.25	0.04

N.B.—(a) = Liquid air trap used.

In each case the gases were dried for two months over phosphorus pentoxide before use. With the inner walls of the vessel coated with paraffin, a millimetre in thickness, the rate of reaction was reduced by 20 per cent. (Expt. 7). This he ascribed to a protective action, preventing the gases from coming into contact with the walls of the vessel, which would hold water vapour.

Hasche suggested that the mechanism of the reaction might be expressed in the form



Briner's Criticisms.—A criticism of Baker's work was levelled by Briner² who described experiments in which nitric oxide and oxygen which had been very carefully dried still reacted. The apparatus which he employed consisted of two bulbs, connected by a tap. The oxygen was introduced into one bulb, and the nitric oxide into the other; the latter had been prepared by the action of sulphuric acid on sodium nitrite solution, and had been purified by low temperature distillation. The gas in one bulb was arranged to be at a slightly lower pressure than the other, so that the gases mixed on opening the tap,

¹ *J. Amer. Chem. Soc.*, **48**, 2253 (1926).

² *J. Chem. Phys.*, **23**, 848 (1926).

in order that it could be observed whether the brown colour of the nitrogen peroxide was obtained or not. The duration of drying in each case varied from three months to a year, a period much longer than was used in Baker's experiments, but in no apparatus did the gas remain colourless. He pointed out that the velocity of combination of nitric oxide and oxygen is greatest at very low temperatures (-183° to -193° C.), where the vapour pressure of water is virtually zero. From this latter fact, and from his experiments, Briner concluded that water, if it does catalyse the reaction, is not necessary for its progress.

Recent Investigations.—This system has also been studied by the present author.¹ The dissociation of nitrogen tetroxide was investigated in two distinct ways. Firstly, nitrogen tetroxide, which had been subjected to fairly thorough preliminary drying, was heated in the presence of phosphorus pentoxide to various temperatures between 250° and 350° C., the resulting gases being analysed; and secondly, the liquid was subjected to intensive drying by continuous distillation through phosphorus pentoxide at about 30° C., and then heated side by side with a comparative tube of "moist" gas of the same colour intensity.

The first investigation led to rather unexpected but extremely interesting complications. At least three reactions occurred simultaneously; the phosphorus pentoxide combined with the nitrogen peroxide yielding an addition compound, the nitrogen peroxide was dissociated into nitric oxide and oxygen to a greater extent than in the "moist" gases, and these products did not recombine on cooling, and thirdly, the nitric oxide decomposed into its elements at a greater rate than normally. This last reaction was probably catalysed by the large surface of the phosphorus pentoxide. The additive compound had been described by Hartung (private communication), who had discovered it just prior to this investigation. The most interesting result, however, from the present point of view is the second. It must be here assumed that the actual intensive drying, i.e. the desiccation necessary to influence the progress of the reaction, took place during the heating process. A tube of gas, initially at a pressure of 264 mm. at room temperature, which had been heated to 250° to 300° C. with phosphorus pentoxide became almost colourless after seven hours. On opening the tip of the tube under very dry mercury, the residual gas pressure was found to be 130 mm., and on the introduction of moisture, the gas immediately turned dark brown and decreased in volume from

¹ *J. Chem. Soc.*, 1928, 1886.

3.02 c.c. to 1.30 c.c. It was concluded that the tubes contained nitric oxide and oxygen and that the moisture caused recombination. Thus Baker's observation of the coexistence of nitric oxide and oxygen gases in the intensively dried state was confirmed. Further, the residual gas was much more dissociated than normal nitrogen peroxide would be on heating to the same temperature. Hence the experiment described above shows that not only does intensive drying inhibit the combination of nitric oxide and oxygen, but that there is some stage in the drying at which the dissociation occurs more readily than the recombination, i.e. when the normal equilibrium is definitely displaced. It is in this respect that moisture behaves in a manner unlike other catalysts. At this particular stage, presumably both reactions are considerably inhibited, but the recombination is hindered to a greater extent than the dissociation. Hence, slowly, the gas becomes more dissociated than it is in the normal "moist" case. This phenomenon will be further discussed when dealing with the ammonium chloride problem.

It was also shown, on the other hand, that when the nitrogen peroxide was dried for some months over phosphorus pentoxide and then heated apart from the drying agent side by side with a specimen of the "moist" gas at the same pressure, the latter became much lighter in colour at 550° C., whereas the "dry" specimen attained its maximum colour intensity at the same temperature as the "moist" gas, but it did not then become lighter again. It retained its dark colour even on heating to 550° C. for twenty-four hours. Thus at the degree of dryness attained in these experiments, the dissociation of nitrogen peroxide into nitric oxide and oxygen must be very slow indeed, even at 550° C.

Summary.—Very carefully dried nitric oxide and oxygen do not react at ordinary temperatures. When the gases are less perfectly dried, the velocity of combination depends on the nature of the walls of the reaction vessel. Intensively dried nitrogen peroxide does not dissociate into nitric oxide and oxygen up to 550° C.

CHAPTER VII.

GASEOUS REACTIONS (*continued*).

THE SYSTEM HYDROGEN CHLORIDE—AMMONIA—AMMONIUM CHLORIDE.

The Combination of Hydrogen Chloride and Ammonia.—

The combination of hydrogen chloride and ammonia at ordinary temperatures seems to be stopped completely in the absence of moisture, although it appears from recent work by Smits that at higher temperatures reaction occurs slowly. The slightest trace of moisture appears to catalyse the reaction, whilst benzene vapour exerts the same effect.¹

Baker gives priority in the discovery of this effect to Helmholtz and Richartz,² but it does not seem at all evident from their communication that they influenced the rate of reaction by this means at all. In the passage to which Baker presumably refers, it is merely pointed out that there is a considerable difference between the appearance of the cloud produced when streams of ammonia and hydrogen chloride gases are allowed to impinge in a jet of steam, and when the gases are allowed to combine before projection into the steam jet. The first to announce that the dry gases did not combine when mixed was Hughes,³ who, however, gave no experimental details, but stated that on blowing out the gas mixture a fume was evident on reaching the outer air, a strong odour of ammonia being observed at the same time.

The subject was studied in detail by Baker.⁴ He dried his ammonia by passage first over solid potash and then over a mixture of cupric oxide and potassium monoxide, and introduced it into one end of a tube divided in the middle by a three-way tap. Dried in this way the ammonia had no apparent action on

¹ Kahlenberg, *J. Physical Chem.*, **6**, 1 (1902).

² *Ann. Phys. Chem.*, **40**, 161 (1890).

³ *Phil. Mag.* (5), **35**, 531 (1893).

⁴ *J. Chem. Soc.*, **65**, 611 (1894).

the phosphorus pentoxide. If, however, the tube had not been carefully dried, the phosphorus pentoxide absorbed the ammonia, forming a hard brown mass, with evolution of heat. Hydrogen chloride was introduced into the other half of the tube. After drying for a week, the gases were allowed to pass through the tap, and mix by diffusion; no white fumes were produced, and there was no decrease in pressure. A trace of moist air caused rapid combination, and mercury rushed up into the tube. He also found that such a dry mixture of ammonia and hydrogen chloride could be partially separated when oppositely charged plates were placed in the mixture, the ammonia passing to the negative plate and the hydrogen chloride to the positive one.

These results were criticised by Gutmann¹ who had repeated Baker's experiment, but with different results. He pointed out that dry hydrogen chloride was absorbed by phosphorus pentoxide; the drier the gas, the more slowly did absorption proceed, advancing rapidly with time, and then finally being retarded. Dry ammonia was also absorbed by phosphorus pentoxide, and at a fairly rapid rate. Gutmann concluded from his experiments that complete desiccation of hydrogen chloride and ammonia was powerless to prevent combination, although the reaction was much retarded and rendered less energetic. In one case as long as half an hour elapsed before the formation of ammonium chloride was complete.

In reply to Gutmann's criticisms, Baker² pointed out that the absorption of ammonia gas by phosphorus pentoxide was not necessarily fatal to the success of the experiment, since the compound formed, diamidopyrophosphoric acid, would serve itself as a drying agent, and if excess of ammonia were added, the gas became dry enough not to react with the hydrogen chloride. In most experiments, however, the phosphorus pentoxide was apparently unaltered, since Baker had taken the precaution of drying the gases very thoroughly before introduction into the apparatus. The ammonia was passed through long columns of freshly ignited lime and was stored over the same reagent. It was found that the presence of even a trace of metaphosphoric acid caused a much more ready absorption of ammonia.

The fact that dry ammonia and hydrogen chloride gases do not react with one another has been confirmed by Tramm.³ He found, however, that there was considerably more difficulty in obtaining ammonia and hydrogen chloride which did not react with phosphorus pentoxide than would be judged from the

¹ *Annalen*, **299**, 3 (1898).

² *J. Chem. Soc.*, **73**, 422 (1898).

³ *Z. physikal. Chem.*, **105**, 397 (1923).

description given by Baker. He was eventually successful in this respect in the case of ammonia, but he could not obtain hydrogen chloride in such a state that combination with the phosphorus pentoxide did not occur. Hence for the drying of this gas he resorted to his low temperature distillation technique. A specimen of such hydrogen chloride was found not to react with the ammonia which had been dried over phosphorus pentoxide when these two gases were mixed. A film of white ammonium chloride appeared immediately a little moist air was allowed to enter into the apparatus.

Some experiments carried out by Burk and Hinshelwood¹ are also of interest in this connection. They dried ammonia and hydrogen chloride "until they were probably drier than the gases in Baker's original experiments; this was indicated by their extremely small rate of absorption by phosphorus pentoxide." They were then mixed in a glass vessel which had been baked out at 200° C. to 300° C. in a high vacuum, i.e. the glass had no moisture which it could give up to the gas, but still held the film of adsorbed water which can only be stripped off by heating in a high vacuum almost to the point of fusion. When the gases were introduced an immediate reaction took place; no cloud of ammonium chloride was formed, i.e. there was no reaction in the gas, but a crystalline deposit spread over the surface of the vessel from the point where the gases entered. Hinshelwood interprets this as showing that the reaction is a heterogeneous one, catalysed by the film of adsorbed moisture on the glass. He also considers that this explains why a trace and no more of moisture is required in order for the reaction to proceed.

The Dissociation of Ammonium Chloride.—Thinking that it would be an excellent method of preparing a dry equimolecular mixture of ammonia and hydrogen chloride, Baker² dried ammonium chloride for a fortnight in soft glass tubes, and heated them to 350° C. for two hours; the ends of the tubes were then broken whilst hot under mercury. The latter rose, on an average, about one-third of the height of the tube. When, however, the ammonium chloride was dried in hard glass tubes and opened under mercury, the tubes were completely filled with that liquid. Thus the ammonium chloride did not dissociate. The vapour density of the dried material confirmed the view, being 26.75 as against a normal value of 13.5.

These results also were criticised by Gutmann,³ as his determinations of the vapour density of carefully dried ammonium

¹ See Hinshelwood, *School Science Review*, No. 31, p. 169 (1927).

² *J. Chem. Soc.*, **65**, 611 (1894).

³ *Loc. cit.*

chloride gave results concordant with complete dissociation. The values he observed after drying over phosphorus pentoxide for periods varying between two and twelve weeks were as follows:

TABLE VIII.

	I.	II.	III.	IV.
Period of drying (weeks) .	2	4	10	12
Vapour density . . .	13.6	13.85	14.75	16.4

Baker,¹ however, criticised Gutmann's method of vapour density determination, in that the gas was collected over water, a few molecules of which might have crept back through his phosphorus pentoxide tube. Even in his later experiments, in which he collected his gases over sulphuric acid, this may have occurred to some extent.

It was pointed out by Abegg² that if Baker's results were to be believed, ammonium chloride when vaporised exerted about an atmosphere pressure at 360° C. whether dissociated or undissociated. In the first case the partial pressure of ammonium chloride molecules is very small, in the latter case it is an atmosphere. He contended that this result was inconsistent with the theory of heterogeneous equilibria, according to which the concentration of the undissociated vapour should, at a given temperature, be independent of the presence of other gases, including the dissociation products.

In order to test this theory, Johnson³ carried out simultaneous vapour pressure and vapour density determinations with ammonium chloride which had been dried for five weeks over phosphorus pentoxide. He confirmed Baker's result, finding that the density of carefully dried ammonium chloride at 345° C. was that of the undissociated compound. The vapour pressure at various temperatures was also determined, that of the undissociated salt in the one case being equal to the sum of the vapour pressures of the dissociation products in the other. This Johnson considered not to be in harmony with the theory of heterogeneous dissociation, but he could suggest no simple explanation.

Treating the problem from the standpoint of thermodynamics, Van Laar⁴ claimed that the conclusions drawn by Abegg and by

¹ *J. Chem. Soc.*, **73**, 422 (1898).

² *Z. physikal. Chem.*, **61**, 455 (1908).

³ *Ibid.*, p. 457.

⁴ *Ibid.*, **62**, 194 (1908).

Johnson were incorrect. He argued that it did not follow that the partial pressure of the undissociated ammonium chloride must always be the same at a given temperature, whatever be the degree of dissociation of the vapour. In the case of the ordinary ammonium chloride, a complete dissociation equilibrium is established; this is not so with dry ammonium chloride, hence he considered that the theory of heterogeneous equilibria is not applicable to this case. He suggested that such dissociation equilibria are defined, not by the partial pressure of the undissociated substance, but by the total pressure in the system.

Abegg¹ in replying to this criticism, maintained that the theory of heterogeneous dissociation equilibria is applicable to the vaporisation of ammonium chloride, since the equilibrium could be attained from either side. Two suggestions were made in explanation:—

(a) That the heat of formation of undissociated gaseous ammonium chloride from solid ammonium chloride may be equal to the heat of dissociation of gaseous ammonium chloride into ammonia and hydrogen chloride.

(b) The molecular weights of the products of vaporisation of sal ammoniac may not be the same in the moist and in the dry states.

This discussion between Abegg and Van Laar continued for some time.²

Wegscheider³ suggested that the fact that ammonium chloride had the same vapour pressure whether wet or moist was only reconcilable with thermodynamics if the solid salt were in different conditions in the two cases. The two, he suggested, might be polymorphous forms, one being changed into the other by the influence of water vapour, or else one form might have a greater internal pressure than the other, this being brought about by an alteration in the surface conditions of one form under the influence of water vapour.

Meanwhile, however, the old fallacy that moist ammonium chloride is completely dissociated into ammonia and hydrogen chloride on vaporisation was being disproved by Smith and Calvert, whose measurements⁴ indicated that the vapour pressure of

¹ *Z. physikal. Chem.*, **62**, p. 607.

² Van Laar, *Z. physikal. Chem.*, **62**, 678 (1908); Abegg, *ibid.*, **63**, 623 (1908); **65**, 36 (1908).

³ *Z. anorgan. Chem.*, **103**, 207 (1908); *Z. physikal. Chem.*, **65**, 97 (1908); **75**, 369 (1911).

⁴ *J. Amer. Chem. Soc.*, **36**, 1363 (1914); **37**, 39 (1915).

chloride so does the vapour density curve. From these results Smits drew the following conclusions :—

(a) In contradiction to Johnson, the vapour pressure of ammonium chloride is lowered by intensive drying.

(b) In opposition to the old theory, the vapour pressure curve of intensively dried ammonium chloride does not coincide with the partial pressure of ammonium chloride, but lies between this and the vapour pressure curve of moist ammonium chloride. (Probably below 260° C. the vapour pressure curve of dry ammonium chloride may actually fall below that of the partial pressure of moist ammonium chloride.)

(c) Intensive drying has not yet stopped the inner transformations, but has caused a marked difference in the inner equilibrium.

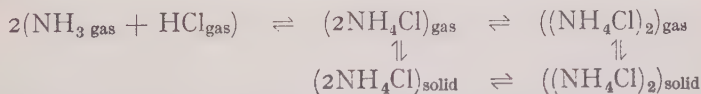
(d) The shift of the inner equilibrium diminished on rise of temperature and disappeared completely above 310° C. This was not due to the liberation of water vapour from the walls, as the curve was traceable repeatedly.

(e) A normal vapour density of 26.75 was found at 286° C., corresponding, on the old theory, to a partial pressure of 3.4 cms. of undissociated molecules, but actually 10 cms. pressure was found in the dry case. This evidently corresponded to a greater number of molecules. This he considered to be possible only if besides NH_4Cl , still larger molecules were present, as well as the dissociation products, ammonia and hydrogen chloride.

(f) The molecular weight became greater than the normal at temperatures below 286° C.; hence association appears, which increases with decreasing temperature.

(g) When $\log P$ is represented as a function of $1/T$, a curved line was obtained. The molecular heat of vaporisation deduced was 64,000 calories at 260° C. and 20,000 at 325° C.

From this evidence, Smits identifies the inactive form of ammonium chloride with $(\text{NH}_4\text{Cl})_2$, so the equilibrium takes the form



He supposes that intensive drying shifts the whole equilibrium in the system from the left-hand side to the right.

This theory has been contradicted recently by Rodebush and Michalek.¹ Experiments carried out by them indicated that

¹ *Proc. Nat. Acad. Sci.*, **14**, 131 (1928); *J. Amer. Chem. Soc.*, **51**, 748 (1929).

intensive drying had no effect on the vapour pressure of ammonium chloride and that the dried chloride showed a normal vapour density corresponding to complete dissociation. The effect which the removal of moisture actually had was to cause a retardation in the rate of evaporation and condensation, several hours being required for equilibrium to be attained. It was suggested that this may have accounted for Baker's anomalous results. They point out that since Smits finds a latent heat of vaporisation of over 40,000 calories per mol. of vapour at $286^{\circ}\text{C}.$, whilst the vapour density corresponds to the molecule NH_4Cl , and since the heat of dissociation of ammonium chloride is 40,000 calories per mol., the dissociation of dry ammonium chloride in the vapour state must be an endothermic reaction.

CHAPTER VIII.

GASEOUS REACTIONS (*continued*).

OTHER GASEOUS REACTIONS.

The System Hydrogen—Bromine—Hydrogen Bromide.—

Although, as has previously been shown, water vapour plays such a fundamental part in the union of hydrogen and chlorine, the evidence is by no means so convincing in the case of hydrogen and bromine.

Bodenstein and Lind¹ stated that they found no change in the velocity of the reaction whether wet or dry, but the details of their experiments reveal that only a very inadequate form of desiccation was employed in their "dry" cases. A negative result was also obtained by Coehn and Tramm,² who found that intensive drying had no effect on the rate of decomposition of hydrogen bromide under the influence of ultra-violet light.

On making calculations from the results of Bodenstein and Lutkemeyer,³ Lewis and Rideal⁴ came to the conclusion that they supported the view that the chemical reaction between hydrogen and bromine takes place through the medium of bromine atoms. Since they had already shown that in the Budde effect the dissociation of excited molecules occurs only in the presence of water vapour, it was anticipated that no reaction would take place in the dry gases. The apparatus they employed in investigating this subject was of the form shown diagrammatically in Fig. 3. It consisted of six glass bulbs, each of 1 cm. diameter and about 6 cm. long. They were connected on one side to *C*, a 20 cm. length of 2 cm. diameter glass tubing into which phosphorus pentoxide could be freshly distilled from the glass bulb *B*, and on the other side to the bromine and hydrogen reservoirs 1 and 2. The hydrogen and bromine reservoirs were separated from

¹ *Z. physikal. Chem.*, **47**, 168 (1906).

² *Ber.*, **56**, 458 (1923).

³ *Z. physikal. Chem.*, **114**, 208 (1924).

⁴ *J. Amer. Chem. Soc.*, **48**, 2554 (1926).

the rest of the system, while the reaction bulbs were being baked out. The remainder of the apparatus consisted of a small phosphorus pentoxide tube to absorb moisture removed during the baking out process, a stopcock, a McLeod gauge with stopcock, a liquid air trap, and a high vacuum pump. The bromine used in all these experiments had been dried over phosphorus pentoxide for nearly a year and a half.

A high vacuum (less than 10^{-6} mm.) was maintained in the apparatus for two days, whilst the reaction tubes were baked out at 420° C. The tubing outside the furnace was frequently and thoroughly baked out with a Bunsen. Fresh phosphorus pentoxide was distilled from *B* to *C*, the former sealed off, and the furnace removed. The phosphorus pentoxide was then distilled into each reaction bulb, so that a thin fluffy layer possessing excellent drying properties coated the surface. The ends were kept free from phosphorus pentoxide, so as to permit the pene-

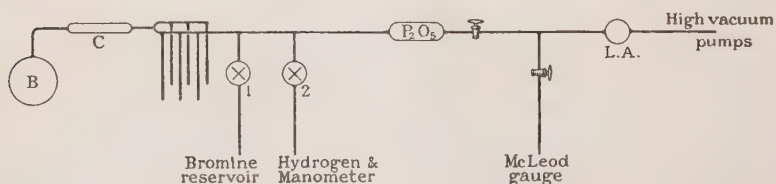


FIG. 3.

tration of radiation from the light source. The pumps at *C* were sealed off after an hour. Bromine was introduced at a known vapour pressure by breaking Seal 1. After an hour this reservoir was sealed off. Similarly, hydrogen was admitted through Seal 2, and the total pressure read. After another day each bulb was sealed off separately.

A bulb was heated to a uniform temperature, and the reaction in some cases accelerated by insolation from a 1000 c.p. lamp. The tip was broken under potassium iodide solution, the iodine liberated being titrated with $N/100$ thiosulphate. The volume of each bulb was determined, and hence the extent to which the reaction had proceeded was deduced.

A series of experiments were first carried out without any phosphorus pentoxide in the reaction vessels, but using dry bromine and dry hydrogen. The results of these experiments are shown in Table IX. In the last column are given the percentages conversion that would be expected from the "moist" thermal reaction, calculated from the data of Bodenstein and

TABLE IX.

Expt.	Press. of Br ₂ mm.	Press. of H ₂ mm.	Temp. °C.	Light on.	Time, hrs.	Conversion Per Cent.	Conversion Per Cent.
1	153	506.1	23.5	yes	42	13.72	—
2	{ 150 131	509.1	100	yes	20.5	11.10	—
3		558	100	yes	12	4.45	—
4	{ 177 180 199 152	399	250	no	2	0.3	6.25
5		399	250	yes	2	1.51	—
6		437	250	no	4	5.33	11.6
7		484.3	250	yes	4	54.5	—
8	{ 184 186 147	452.3	275	no	4	45.8	52.2
9		450.3	275	yes	4	82.6	—
10		512.1	275	no	4	56.9	—
11	{ 140 221 167	463.4	300	yes	2	56.0	ca. 52.2
12		415.3	300	no	1	42.3	61.3
13		469.3	300	yes	1	79.4	—

Lind.¹ If the two series of data can be fairly compared, it would appear that the preliminary drying given to the reactants caused a very considerable retardation of the reaction.

When the phosphorus pentoxide was present with the bromine and hydrogen in the reaction tubes, however, both the thermal and photochemical combination were stopped completely at low temperatures. At high temperatures the rate of combination was negligible compared with that of the wet gas. The results obtained are given in Table X.

TABLE X.

Original Pressure.		Temp. °C.	Time, hrs.	Final Pressure Br ₂ (mm.)	Conversion Per Cent.	Conversion, Wet, Per Cent.
Br ₂ (mm.)	(H ₂ mm.)					
151	468	275	4	153	Nil	67.5
151	468	325	3	147	2.6	100 in 1 hr.
151	468	400	2	142.6	5.56	100 in 5 mins.

They suggested that the primary mechanism of the reaction between hydrogen and bromine was as follows:—

(a) The formation of excited molecules of bromine by collision.

¹ *Loc. cit.*

(b) Dissociation of these excited molecules into atoms on collision within their mean lifetime with water molecules.

(c) Reaction of atoms with hydrogen molecules, or (more rarely at a high hydrogen pressure) with bromine atoms. By calculations of the mean life period of the excited bromine molecules they come to the conclusion that a water vapour pressure of 0.1 mm. gives the maximum velocity to the reaction.

The second series of Lewis and Rideal's experiments, however, have been shown to be valueless, since Bodenstein and Jost¹ have found that when hydrogen and bromine are heated with phosphorus pentoxide a chemical reaction occurs, resulting in the formation of phosphorus pentabromide. This affects the results shown in Table X. but not those in Table IX., which remain so far the only evidence that moisture exerts any influence whatever on the reaction between bromine and hydrogen.

The System Hydrogen—Iodine—Hydrogen Iodide.—It was observed by Coehn and Tramm² that hydrogen iodide dissociated under the influence of ultra-violet light even when carefully dried.

This system was also investigated by Lewis and Rideal,³ using an apparatus of the same type as they employed for the investigation of the combination of hydrogen and bromine. After drying for a few weeks, hydrogen iodide was introduced into bulbs lined with sublimed phosphorus pentoxide at a known pressure. The bulbs of gas were sealed off at this pressure and heated to a known temperature for a known period. The tubes were then opened and analysis for iodine carried out in the usual way. The following results were obtained:—

TABLE XI.

Temp. °C.	Time.	Original Pressure of HI (mm.)	HI Decomposition, mm.	Decomposition, Per Cent.
432	1 hour	404	396	98
			402	99.5
			356	88.0

At this temperature the equilibrium value for the moist material corresponds to about 19.5 per cent. decomposition; hence Lewis and Rideal deduced that the equilibrium was completely shifted over to the dissociated side on intensive drying.

¹ *J. Amer. Chem. Soc.*, **49**, 1416 (1927).

² *Ber.*, **56**, 458 (1923).

³ *J. Amer. Chem. Soc.*, **48**, 2554 (1926).

It was pointed out by Bodenstein and Jost,¹ however, that if this result were to be believed, perpetual motion would be attained, thus (a) introduction of a trace of water into dry, completely dissociated hydrogen iodide would change the system into one of 21 per cent. dissociation with work performed; (b) on removal of water, 99 per cent. dissociation would once more be obtained, with performance of work again.

They found experimentally that the hydrogen iodide reduced the phosphorus pentoxide, yielding iodine, which accounted for the apparent 99 per cent. dissociation obtained by Lewis and Rideal.

It has recently been stated by Kistiakowsky² that the rate of decomposition of hydrogen iodide is not influenced by extreme drying. In order to investigate how far the rate of the thermal decomposition of hydrogen iodide was dependent on the presence of traces of water vapour, experiments were carried out with a hydrogen iodide purification apparatus in which taps had been eliminated, being replaced by internal seals. All the separated parts of the charging apparatus were baked out in a vacuum at 450° to 400° C. for ten hours. The quartz part of the apparatus including the reaction bulbs was heated to a somewhat higher temperature than the rest, to which it was connected by a graded seal. Hydrogen iodide was distilled four times in a vacuum from a bath of melting carbon disulphide (— 112° C.), only the first fraction being used each time and the rest being sealed off after cooling. He supposed that the hydrogen iodide prepared in this way would be both extremely dry and very free from foreign matter. The results, however, were similar to those obtained when fewer precautions were taken. From the description given, it is evident that the hydrogen iodide was by no means intensively dried however, as no desiccating agent was used, the drying being dependent only on the distillation from the low temperature bath.

Hydrogen and Nitrous Oxide.—No actual experiments appear to have been made upon the influence of moisture on the reaction between hydrogen and nitrous oxide alone, but the following experiments by Baker suggest that a very pronounced effect will probably be observed. Baker³ found that nitrous oxide and hydrogen react slowly and uniformly at 530° C.; the moist reaction was much accelerated by lime and more by

¹ *J. Amer. Chem. Soc.*, **49**, 1416 (1927).

² *Ibid.*, **50**, 2315 (1928).

³ *Mem. Manchr. Soc.*, **53**, No. 16 (1909); *Chem. News*, **99**, 126 (1909).

thoria, whilst in the presence of radium bromide explosion occurred. After ten days' drying by phosphorus pentoxide in the presence of thoria, no measurable combination occurred on heating for five minutes at 530°C . Hence it was concluded that in the presence of moisture, increased ionisation increases the rate of chemical change, whilst it has no effect in the absence of moisture. This Baker supposed to support Sir J. J. Thomson's Theory¹ since the increase in the number of ions increases the number of nuclei upon which the water vapour can condense.

Carbon Monoxide and Nitrous Oxide.—It was shown by Dixon² that when carbon monoxide and nitrous oxide are mixed in equal volumes over mercury in the ordinary way, they are readily exploded by a spark. When well dried, however, they resist the action of the spark; the addition of a trace of water renders them explosive again.

Addition of carbon disulphide vapour to the carbon monoxide-nitrous oxide mixture causes some reaction to proceed, the extent to which the carbon monoxide is oxidised depending on the proportion of the disulphide added. Thus with 2.5 per cent. carbon disulphide, the mixture did not inflame, but with 2.8 per cent. a flame was produced which traversed the tube. Over 90 per cent. of the carbon monoxide remained unburnt, however, together with some carbon disulphide.

Similarly, it has been found³ that if mixtures of carbonyl sulphide and nitrous oxide were allowed to stand for some weeks over pure sulphuric acid and then for a further lengthy period over phosphorus pentoxide, an electric spark produces no explosion, whereas if a drop of water be then added a violent explosion takes place. Hence nascent carbon monoxide does not seem to react at all readily with dry nitrous oxide.

Oxygen and Ozone.—The extent to which traces of moisture can influence the formation and decomposition of ozone has been by no means fully investigated. The data on the subject are extremely conflicting, and considerable further research in this system seems to be necessary before any definite conclusions can be drawn.

The first investigators to attempt any experiments on this subject were J. J. Thomson and Threlfall,⁴ who sealed up air free from ozone, together with phosphorus pentoxide, in an ozoniser. After three months an electric discharge was passed through it, but ozone was produced in large quantities. Hence it was con-

¹ See page 142.

² *J. Chem. Soc.*, **69**, 774 (1894).

³ Russell, *ibid.*, **77**, 361 (1900).

⁴ *Proc. Roy. Soc.*, **40**, 342 (1886).

cluded that ozone was produced when an electric spark was passed through very carefully dried oxygen. This was confirmed soon afterwards by Shenstone and Cundall¹ and later by Baker.² The former authors found that when Siemen's ozonisers were used, the proportion of ozone seemed to be greater than when less pure oxygen was employed. Dry ozone was completely destroyed by contact with mercury for some hours without any perceptible oxidation of the mercury surface.

The subject was further investigated by Shenstone³ who found that with a given apparatus the proportion of ozone formed was 13.3 to 13.6 per cent. of the oxygen submitted to the discharge when moist, and only 11.1 per cent. when moderately dry. He thought that drying diminished the stability of ozone, for whilst moist oxygen well charged with ozone lost the latter so slowly that measurements could not be carried out, in carefully dried oxygen the ozone decomposed so rapidly that it was difficult to measure the exact proportion present. Moderately dried oxygen gave an intermediate result. With some oxygen which had been dried as carefully as possible, it was thought that only about 0.2 per cent. of ozone was formed, so the conclusion was drawn that dried oxygen ozonises very badly.

However, it was pointed out by Armstrong that Shenstone probably included any nitrogen peroxide (formed from residual nitrogen in his oxygen) at the same time in his ozone determinations. This would also account for the peculiar instability of his dry ozone. This view received support from Chapman and Jones,⁴ who showed that oxides of nitrogen could exert the effect observed by Shenstone. As a result of a large series of experiments, they also concluded that small quantities of water vapour do not exert any great influence on the thermal decomposition of ozone. On the other hand, they thought it quite probable that in large quantity it might be a weak catalyst. This would be expected if ozone be assumed to be slightly acidic, as is indicated by its action with strong alkali, presumably a reaction of the type



At the same time other investigators have still found that both the formation and decomposition of ozone are influenced by the presence of traces of moisture. Warburg and Leithauser⁵ found that the formation of ozone, both in oxygen and in air, is reduced by the presence of water vapour, the effect being greater

¹ *J. Chem. Soc.*, **51**, 610 (1887).

² *Ibid.*, **65**, 611 (1894).

³ *Ibid.*, **71**, 471 (1897).

⁴ *Ibid.*, **99**, 1811 (1911).

⁵ *Ann. Physik.* (iv.), **20**, 757 (1906).

in oxygen than in air. They thought at that time that the rate of decomposition was unaffected by moisture. In Warburg's later experiments,¹ however, he found that the photochemical deozone action was approximately twice as large in moist oxygen-ozone mixtures as in the corresponding dry mixtures. The spontaneous decomposition of ozone also appeared to be increased by the presence of water vapour.

In contradiction to this evidence, however, the most recent work on this subject, carried out by Tramm² indicates that the formation of ozone is independent of the moisture content when this is varied between 0.004 mm. and 10 mm.

It is highly probable that the results of the earlier investigators were due to the presence of impure phosphorus pentoxide. It is now well known that ozone is rapidly destroyed by impure phosphorus pentoxide, probably owing to the presence of lower oxides.

The Combination of the Halogens with Ethylene.—As has been mentioned in Chapter II., Regnault³ was the first to show that dry chlorine did not combine with dry ethylene in diffused daylight. He says " . . . j'ai remarqué que la réaction du chlore sur l'hydrogène bicarboné n'avait pas lieu quand les deux gaz étaient parfaitement secs, au moins à la lumière diffuse."

That these reactions occurred mainly on the walls of the vessel was first found by Stewart and Edlund,⁴ who showed that dry ethylene and dry bromine do not combine at 0° C. in the gaseous phase but only on the walls of the vessel.

Norrish⁵ attributed the catalytic effect of moisture on the combination of these compounds to the polarity of the walls of the vessel. He showed that dried ethylene and bromine practically ceased to react when enclosed by non-polar walls of paraffin wax; ethylene dibromide was formed only slightly in the cracks of the wax. On the other hand, the gases reacted rapidly when enclosed in a vessel with a " polar " surface of glass, stearic acid, or cetyl alcohol. The mean values of the bimolecular reaction coefficient found by Norrish are given in Table XII.

An ammoniated surface is rather more active than the bare glass wall. A convincing form of experiment described by Norrish consisted in passing dry ethylene and dry bromine through a

¹ *Sitzungs. K. Akad. Wiss.*, 1913, 644.

² *Z. physikal. Chem.*, **105**, 356 (1923).

³ *Ann. Chim. Phys.* (ii.), **69**, 171 (1838).

⁴ *J. Amer. Chem. Soc.*, **45**, 1014 (1923).

⁵ *J. Chem. Soc.*, **123**, 3006 (1923).

paraffined tube and then through a glass tube. No ethylene dibromide was observed in the paraffined tube, whereas about 0.3 gram collected in the glass tube.

TABLE XII.

	k.
Glass . . .	0.0506
Stearic acid . . .	0.0864
Paraffin wax . . .	0.0030
Cetyl alcohol . . .	0.0266

Similar phenomena are observed in the reaction between ethylene and chlorine.¹ A very carefully prepared paraffin wax surface showed a reactivity 1200 times smaller than that of glass. Water vapour at a partial pressure of 6 mm. increased the reactivity of the glass by 30 per cent., but did not affect the paraffin wax surface. The comparative reactivities of the different surfaces were :—

Glass.		Stearic Acid.	Paraffin Wax.
Gas Dry.	Gas Wet.		
1.0	1.3	1.06	0.0008

The Catalytic Combination of Sulphur Dioxide and Oxygen.

—The influence of moisture on the union of sulphur dioxide and oxygen using manganese dioxide as a catalyst was investigated by Russell and Smith,² who found that this reaction was entirely stopped on the removal of water vapour. The apparatus they employed was of the type shown in Fig. 4. This was previously dried by heating in a large flame in a current of dry air. The mixture of

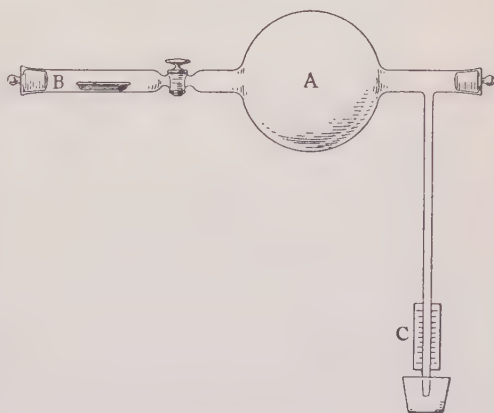


FIG. 4.

¹ Norrish and Jones, *J. Chem. Soc.*, 1926, 55.

² *J. Chem. Soc.*, 77, 346 (1900).

sulphur dioxide and oxygen was then introduced into bulb *A*, when it was allowed to dry over distilled phosphorus pentoxide, whilst the manganese dioxide was dried over phosphorus pentoxide in an atmosphere of oxygen in the small tube *B*. The stoppers were lubricated with phosphorus pentoxide, and coated on the outside with a mixture of beeswax and vaseline to keep out moisture. After a few days' drying, the tap connecting the two was turned, but eight days later no change in volume was observed, although the moist gases combine readily under these conditions.

Similarly it was found that heated platinised pumice caused no combination of the dried gases in five hours, but in twenty-four hours an appreciable diminution was noticed. The authors made the observation that the platinised pumice was very difficult to dry. It was found that the introduction of steam caused rapid reaction.

Sulphur Dioxide and Ammonia.—It was first observed by Divers and Ogawa¹ that, although sulphur dioxide and ammonia, even when comparatively well dried, unite at once and with great energy, yet if sufficient care has been taken to exclude moisture, they do not combine. As sulphur dioxide could be dried better than ammonia when commercial phosphorus pentoxide was used as the drying agent, they were only successful in mixing the gases without combination when the sulphur dioxide was introduced into the vessel first. The preparation flask, with its tubes, was heated, and kept for a time in a desiccator. It was then placed in ice and salt, and a slow current of sulphur dioxide passed slowly through it, the gas having been dried by passage first through tubes of sulphuric acid and then of phosphorus pentoxide. The outlet tube dipped into mercury. Ammonia, dried first by cooling in a freezing mixture, and then by passage through long tubes containing freshly fused and crushed potash, was also passed slowly into the flask. The interior remained clear for some minutes, the mixed gases combining only on their escape through the mercury into the air, with the production of white fumes; but after a time, the ammonia having, presumably, gradually brought in moisture with it, owing to its more rapid passage through the drying tubes, the walls of the flask became suddenly coated with an orange coloured deposit. Under these conditions, two volumes of ammonia united with one of sulphur dioxide, forming ammonium amidosulphite ($\text{NH}_4\text{SO}_2(\text{NH}_2)$).

¹ *J. Chem. Soc.*, **77**, 327 (1900).

The System Sulphur Dioxide—Chlorine—Sulphuryl Chloride.

—The reaction between sulphur dioxide and chlorine appears to be very strongly dependent on the presence of water vapour. It was found by Le Blanc¹ that the removal of water vapour stopped the dark reaction, which was fairly rapid in the presence of water vapour. Similarly, Coehn and Tramm² found that the photochemical reaction in visible light was completely inhibited by the protracted drying of the gases, no appreciable reaction occurring in four hours when dry, whereas 45.4 per cent. combination occurred between the moist gases during the same period of time and under the same conditions.

The System Carbon Monoxide—Chlorine—Carbonyl Chloride.

—It has been observed by Wildermann,³ Bodenstein,⁴ and Coehn and Tramm² that the velocity of the photochemical combination of carbon monoxide and chlorine was greatly reduced by thorough desiccation of the gases, but that the process invariably occurred at an appreciable rate; thus the last-named authors found that 22.2 per cent. conversion occurred in forty-eight minutes with the dried material, whereas with the moist gases under similar conditions 91 per cent. combination occurred in fifteen minutes.

Hydrogen Sulphide and Oxides of Nitrogen.—Higgins⁵ found that there was no reaction between hydrogen sulphide and "nitrous gas" when these gases were dry. He states that:—

"In one experiment, when equal parts of sulphuretted hydrogen and nitrous gas, which stood separately over dry mercury for several days, were mixed, no decomposition took place, although the mixture was suffered to stand for three weeks. When water was sent up, the whole of the gases except a large bubble of azote, disappeared in the course of seven days. The water contained no free acid or ammonia, but a little ammonium nitrate remained on evaporating."

Later⁶ it was shown by Leconte that dry nitric oxide and hydrogen sulphide do not react.

Hydrogen Sulphide and Sulphur Dioxide.—It appears to have been first shown by Cluzel⁷ that moisture plays a very important part in the interaction between gaseous hydrogen sulphide and sulphur dioxide. He found that when both these

¹ *Z. Electrochem.*, **25**, 229 (1919).

² *Ber.*, **56**, 458 (1923).

³ *Z. physical. Chem.*, **42**, 257 (1903).

⁴ *Rec. trav. Chim.*, **41**, 585 (1922).

⁵ *Experiments and Observations on the Atomic Theory*, Dublin, 1814, p. 142.

⁶ *Ann. Chim. Phys.* (3), **21**, 180 (1847).

⁷ *Ibid.*, **84**, 113 (1812).

gases had been dried over calcium chloride and were then introduced into bell-jars, they might remain for any period from a quarter of an hour up to three or four hours according to the completeness of the drying before any visible deposition of sulphur took place. Reaction always occurred, however, and when once commenced continued rapidly. No difference was observed whether the jar was kept in darkness or exposed to the light. On the other hand, when a piece of moistened paper was introduced into the bell-jar, reaction occurred rapidly. Cluzel considered that the mercury over which the gases were enclosed contained a little moisture, which served to start the reaction. The latter then itself produced sufficient moisture to enable it to go to completion.

Similar observations were made by de Luca and Ubaldini¹ and by Schmidt.² However, they seem to have been able to carry the matter a step further forward and stopped the reaction completely. A convenient method of showing this effect of removing the moisture from a mixture of hydrogen sulphide and sulphur dioxide as a lecture experiment is described by Noyes and Sammet.³

Baker⁴ found that hydrogen sulphide and sulphur dioxide can be kept unchanged even if water vapour is present in some quantity, but that if liquid water be introduced the separation of sulphur is immediate. It was also found that if a small tube of radium bromide were placed in such a mixture and allowed to stand for some time, the whole of the gases condensed as sulphur and water in the small tube containing the salt. Baker considered that the water vapour condensed, momentarily at any rate, in liquid drops on the ionised particles in the radium bromide tube, and in the presence of these drops the reaction between the gases is rapid and complete. He also pointed out that liquid alcohol and liquid sulphur dioxide, both with a high dielectric constant, can bring about decomposition in the mixture, whilst chloroform, of which the dielectric constant is low, is inert. Metallic aluminium and mercury were also found to be unable to effect the change.

It was found by Klein⁵ that water in its ability to accelerate this reaction is in no way exceptional or unique, since other liquids were observed to possess the same power. The gases were dried until no combination took place on mixing and allow-

¹ *Compt. rend.*, **64**, 1200 (1867).

² *Z. Chemie*, **11**, 50 (1868).

³ *J. Amer. Chem. Soc.*, **24**, 498 (1902).

⁴ *Chem. News*, **99**, 126 (1909).

⁵ *J. Physical Chem.*, **15**, 1 (1911).

ing the mixture to stand. A small amount of an organic liquid which had been dried carefully over phosphorus pentoxide was then added. Of the liquids investigated, the following induced the reaction: ethyl, isoamyl, and isobutyl alcohols (all immediately); acetone (immediately); methyl ethyl ketone (in less than two minutes); acetonitrile (in fifteen minutes); propionitrile (in seven minutes); valeronitrile (in fifteen minutes); benzyl cyanide (in two minutes); methyl benzoate (in twenty-five minutes); propyl acetate (immediately); isobutyl acetate (six minutes); ether (less than two minutes); benzaldehyde (immediately); and carvone (immediately).

On the other hand, the following liquids produced no action: carbon disulphide, ethyl disulphide, benzene, amylene, chloroform, carbon tetrachloride, ethyl chloride, acetyl chloride, benzoyl chloride, and nitrobenzene. Klein concluded that there is no rigorous parallelism between the dielectric constant or the association of the liquid on the one hand and its ability to induce action on the other, but that the only rational explanation lay in the view that chemical reaction occurs through the formation of intermediate compounds.

Carbonyl Sulphide and Nitrous Oxide.—It was found by E. J. Russell¹ that if mixtures of carbonyl sulphide and nitrous oxide were allowed to stand for some weeks over pure sulphuric acid and then for a further lengthy period over phosphorus pentoxide, an electric spark produced no explosion. On then decanting the mixture into a eudiometer and adding a drop of water a violent explosion took place.

Sulphur Dioxide and Nitric Oxide.—Numerous experiments carried out by Lunge² showed that dry nitric oxide and sulphur dioxide did not react either at ordinary temperatures or at higher temperatures of 50° and 100° C., so long as moisture and air were excluded.

The Photochemical Reactions between the Hydrogen Halides and Oxygen.—The influence of moisture on these reactions was investigated in some detail by Richardson.³ He filled two bulbs with hydrogen chloride and oxygen in the ratio of four volumes of the former to eight of the latter, i.e. with considerable excess of oxygen. The gases were dried thoroughly over phosphorus pentoxide. After sixty-three days exposure to sunlight, no trace of free chlorine could be detected when the gases were absorbed in water and tested with potassium iodide, or on

¹ *J. Chem. Soc.*, **77**, 361 (1900).

² *Ber.*, **14**, 2196 (1881).

³ *J. Chem. Soc.*, **51**, 801 (1887).

analysis. With the wet gases, in twenty-one days 73·81 per cent. of the chlorine was liberated as free chlorine.

Wet hydrogen chloride and dry oxygen were next mixed, so that the mixture was only partially saturated with water vapour. After sixty days no trace of chlorine was detected. Hence it was concluded that a mixture of hydrogen chloride and oxygen was quite stable even in the presence of water vapour, provided that liquid water was absent. Richardson supposed that the gases in the "wet" cases had deposited moisture on the slightest temperature change, thus providing the liquid water necessary in order to start the reaction.

Similarly, Richardson found that dry hydrogen bromide and oxygen did not react in sunlight. On the other hand, hydrogen iodide reacted with oxygen even when both gases were dried.

The Combustion of Carbon Disulphide.—Only one series of experiments are recorded in the literature, but it would appear from this that the combustion of carbon disulphide can occur without the intervention of water vapour. Baker¹ found that pure carbon disulphide vapour which had been sealed up with three times its volume of dried oxygen in the presence of phosphorus pentoxide for either twelve days or six weeks exploded with equal force to a moist mixture, both when sparked electrically and when heated. An explanation suggested is that decomposition must begin before interaction with oxygen can take place, decomposition beginning at 216° and explosion at about 260° C.² He supposed that, although he had shown previously that neither of these elements is combustible in dry oxygen in the normal way (see pp. 87 and 91), they must be able to combine directly with oxygen when in the nascent state without the intervention of water.

Carbon Dioxide and Ammonia.—It was mentioned by van't Hoff³ that the formation of ammonium carbamate from carbon dioxide and ammonia gases proceeds much more slowly in the absence of moisture than when a little is present. Later,⁴ it was found by Hughes and Soddy that ammonia, carefully dried by means of soda-lime, solid caustic soda, and ignited lime, and carbon dioxide which had been carefully dried by means of sulphuric acid and phosphorus pentoxide, did not react when they were mixed, and when blown out of the tube the gas both smelled of ammonia and gave a precipitate with lime water.

¹ *Phil. Trans.*, **179A**, 571 (1888).

² Baker, *J. Chem. Soc.*, **65**, 611 (1894).

³ *Studien über chemische Dynamik*, Amsterdam, 1884.

⁴ *Chem. News*, **69**, 138 (1894).

The Interaction of Hydrocarbons with Oxygen.—Experiments carried out by Bone and Andrew¹ indicate that dried mixtures of ethylene, acetylene, or ethane with oxygen react quite as readily as the moist mixtures. Considering the results as a whole, one has some evidence that the initial rate of reaction is slightly greater in the dried than in the undried gases, ignition, when it occurred, always commencing in the dried tube first.

¹ *J. Chem. Soc.*, 89, 652 (1906).

CHAPTER IX.

SOLID-GAS REACTIONS.

OXIDATION OF SOLIDS.

IN approaching the branch of the subject dealing with reactions between solid and gaseous phases, one is faced with an extremely complex chain of circumstances. It seems hardly likely that the effect exerted by moisture on these reactions can be actually the same as that encountered in certain gaseous reactions, but so little is known yet of the mechanism of any of these reactions that it does not seem possible to distinguish between the different mechanisms by which water vapour can exert an influence in determining the progress of a chemical reaction. In general, a much greater amount of water vapour is required to catalyse a reaction between a solid and a gas than that which usually suffices for gaseous reactions. As in the case of gaseous reactions, no very satisfactory explanation has yet been put forward to account for the influence of moisture on many of these systems.

Manganese and Oxygen.—In quite early days it was observed by Bergmann¹ that moisture exerts a great influence on the atmospheric corrosion of manganese.

“The regulus [of manganese] when fused generally persists in a dry place, but sometimes undergoes spontaneous calcination and falls into a brownish-black powder which is somewhat heavier than the perfect metal, moisture and acidic air aid this process. A small piece put into a dry bottle well corked remained perfect for six months, but afterwards exposed to open air for two months contracted a brownness on its surface, together with so much friability as to crumble between the fingers. The internal parts, however, retained an obscure metallic splendour, which disappeared in a few hours.”

¹ *Physical and Chemical Essays*, English Trans. (1786), Volume II., p. 204.

Iron and Oxygen.—Also before the end of the eighteenth century it was observed by William Higgins that moisture had an important effect on the oxidation of iron.¹ He stated that

“When iron is moistened with water and confined in a glass jar over mercury, it will yield hydrogen. Iron under the same circumstances in oxygen gas will give no hydrogen; the oxygen is condensed; in both cases the surface of the iron is equally oxidised.

“Iron and dry oxygen gas, kept in contact ever so long will not act on each other; the iron preserves its metallic brilliance and the gas its elastic state, and no hydrogen is evolved. Hence it appears that iron has no effect on oxygen gas in a common temperature, and that it is the oxygen of the water which unites to it, whilst the oxygen of the gas is condensed by the liberated hydrogen in its nascent state so as to reproduce water. This is effected by a double influence which is so obvious as not to require an explanation. This modification of chemical affinity escaped the observation of chemists before I had written. The process of bleaching is effected in this way.”

It was also observed by Bonsdorff² that iron was not oxidised when it was brought under a bell-jar containing air dried by means of sulphuric acid, whereas it slowly corroded in moist air.

On the other hand, it has been shown by Friend³ that iron yields its characteristic tempering colours when heated in dry air or oxygen.

Alkali Metals and Oxygen.—It was found by Bonsdorff⁴ that even sodium and potassium remained quite unchanged in air dried by sulphuric acid. He remarked that it was more difficult to demonstrate this property satisfactorily in the cases of these two metals than with the other metals he employed (arsenic, bismuth, lead, zinc, cadmium, iron, and copper). The difficulties encountered in the investigation were overcome in the following manner. Potassium was melted in nitrogen, and then the nitrogen replaced by air which had been dried over sulphuric acid and caustic potash. The potassium remained unchanged and did not lose its metallic lustre. Again, in 1872, it was observed by Ariens Kappers⁵ that sodium and potassium did not

¹ *Comparative View of the Phlogiston Theory* (1791), p. 11; *Experiments and Observations on the Atomic Theory*, Dublin, 1814, p. 52.

² *Ann. Phys. Chem.*, **41**, 293 (1837).

³ *J. Iron and Steel Inst.*, **2**, 172 (1909).

⁴ *Ann. Phys. Chem.*, **41**, 293 (1837).

⁵ *Dissertation*, Groningen, 1872.

oxidise in dried oxygen, but the discovery does not appear to have been at all widely published.

The reactions were first studied in detail by Holt and Sims,¹ who found that when two towers of sulphuric acid were used for drying a stream of air, the oxidation of potassium occurred only slowly in it. Hence further experiments were carried out in order to test whether this metal could resist the action of oxygen from which all the moisture had been removed. A tube of thick glass was constricted so as to form two chambers; a sealed glass bulb containing potassium was introduced into the smaller chamber, and phosphorus pentoxide into the larger. The tube was filled with oxygen, sealed, and allowed to remain for some weeks. By now shaking the tube, the glass bulb containing the potassium was broken, and the metal exposed. The bright surface remained absolutely unaltered at ordinary temperatures, even when left for some days. Subsequently, heat was applied until the potassium fused and even vaporised, but no trace of oxidation occurred. It is evident, therefore, that potassium can be distilled in very dry oxygen without any oxidation taking place. It was further shown that if a cylinder into which phosphorus pentoxide had been introduced were inverted over mercury, and left for some days until the moisture was removed, freely burning potassium on a deflagrating spoon was instantly extinguished in the dry gas, but on raising the spoon out of the cylinder it was re-ignited. Even when dried only by calcium chloride, it was found that oxygen attacked potassium only slowly, even at 200° C.

Similarly if air or oxygen is dried fairly well, it becomes increasingly difficult to get sodium to ignite in it. Sodium does not burn in very dry oxygen. Holt and Sims found that when a small amount of sodium was placed in an atmosphere of dried oxygen, as in the case of potassium, the surface of the metal remained perfectly bright at ordinary temperatures, nor was there any sign of oxidation even on heating the tube until the metal began to vaporise. It was further shown that if dried oxygen were led into molten sodium at 235°, no oxidation occurred except at the surface, and when the tube conducting the oxygen was taken out of the molten sodium and raised to the mouth of the tube containing the latter, the sodium adhering to it immediately took fire, but was extinguished again on lowering it into the tube.

Calcium and Oxygen.—According to Erdmann and van der Smissen,² calcium is not oxidised in dry oxygen.

¹ *J. Chem. Soc.*, **65**, 432 (1894).

² *Ann.*, **361**, 31 (1908).

Mercury and Oxygen.—The investigation of the influence of water vapour on reactions in which mercury takes part is always interesting, because none of these reactions seem to cease on the removal of moisture. The combination with oxygen appears to be no exception to this rule, since Purcell¹ could detect no change in the velocity of reaction between mercury and oxygen whether moist or dry. It appears unlikely that this result was due to inefficient drying, as the care taken in manipulation may be judged from the following experimental details. Fifty cubic centimetres of pure mercury were placed in bulb *A* (Fig. 5). Some pure phosphorus pentoxide was introduced into the side tube *B*, which was at once sealed off. The apparatus was baked out under vacuum and then sealed off at the constriction *D*. During the period of drying, the mercury in *A* was heated so that it continuously distilled and condensed in the upper part of the tube. Samples were sealed off in *C*, *C'*, and these sealed into larger tubes. Dry oxygen was introduced to a little below atmospheric pressure, and the tube sealed off and heated to 450° C. to accelerate drying, the phosphorus pentoxide being cooled. After ten days, drying was continued at room temperature. Each tube was examined by drawing off the phosphorus pentoxide bulb and breaking the tube of mercury; it was then heated together with a damp comparison tube at 400° for half an hour, and the amounts of oxide formed compared. He concluded that the accumulation of negative results for mercury and its compounds shows that they can react in the presence of unusually small amounts of water.

Carbon and Oxygen.—In the course of some organic combustions, Dubrunfaut² found that carbon did not burn so readily in oxygen dried by strong sulphuric acid as it did if the oxygen were moist. Similar effects were observed when the carbon was mixed with dry cupric oxide. He ascribed the incompleteness of

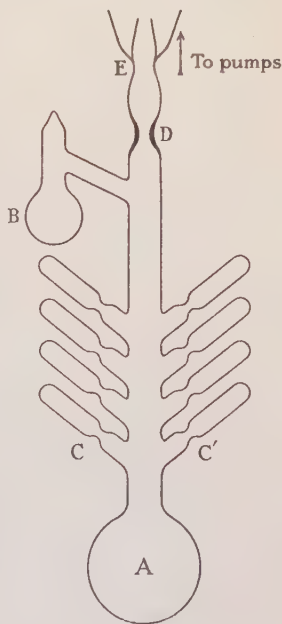


FIG. 5.

¹ *J. Chem. Soc.*, 1928, 1207.² *Compt. rend.*, **73**, 1395 (1871).

the combustion to the necessity of the presence of water in undetectably small amounts, which acted as intermediaries, supposing that the carbon attacked the water liberating hydrogen and that the latter then burnt. It was concluded that carbon would be totally incombustible in oxygen which was completely dry, if such were possible.

This observation was severely criticised by Dumas,¹ as on repeating the experiment with a large quantity of partially dried oxygen, from which 7 mgms. of water were absorbed from 50 litres of gas by sulphuric acid, he was able to burn the whole of a small quantity of carbon. The latter was prepared by purifying native graphite by fusion with potash, washing with water, and boiling with dilute hydrochloric acid, and then heating to whiteness in dry chlorine. It was transferred whilst hot to a glass tube which was exhausted and combustion performed in a stream of oxygen dried by passage over caustic potash and sulphuric acid. The carbon was completely burnt, 7.0635 grams, combining with 18.8095 grams of oxygen.

That the presence of moisture does exert a considerable influence on the combustion of carbon was finally proved by Baker.² Wood charcoal was freed from hydrogen by heating in a current of chlorine for several hours. It was then placed in glass tubes into which phosphorus pentoxide had been introduced. In some cases the two substances were separated by a disc of platinum foil, which was not, however, so close fitting as to prevent the free diffusion of the gaseous contents of the tubes. Oxygen dried by means of sulphuric acid was then passed through the tubes, which were then sealed at both ends. The ends of the tubes containing the carbon were placed in an air bath at 130° to 150° C. during drying, whilst the phosphorus pentoxide was kept cool. After standing for some days, each tube was heated side by side with a similar tube containing charcoal in moist oxygen in a large flame. The moist carbon always burnt with scintillation, but the dry carbon was apparently unaltered. Analysis showed, however, that some combustion had occurred. Table XIII. gives the results of the analysis of the gaseous contents of the tubes after heating to redness for about two minutes.

In another series of experiments, a mixture was made of platinum black and very carefully purified charcoal. Hard glass tubes were slightly constricted in the middle and heated in a current of dry air to dull redness in order to remove the moisture.

¹ *Compt. rend.*, **74**, 137 (1872).

² *J. Chem. Soc.*, **47**, 349 (1885); *Phil. Trans.*, **179A**, 571 (1888); *Proc. Roy. Soc.*, **45**, 1 (1888).

TABLE XIII.

		CO ₂ .	CO.	O ₂ .	N ₂ .
I.	Wet	50.1	22.2	—	27.6
	Dried 1 week	15.4	20.6	41.3	22.6
II.	Wet	51.0	31.2	—	17.7
	Dried 2 weeks	19.0	14.8	46.1	20.0
III.	Wet	45.3	32.5	—	22.1
	Dried 3 weeks	14.1	27.8	28.2	29.8
IV.	Wet	23.3	60.0	—	16.6
	Dried 4 weeks	12.5	27.5	39.0	21.0
V.	Wet	58.8	23.2	—	17.9
	Dried 5 weeks	15.8	24.2	33.3	26.6
VI.	Wet	52.4	24.2	—	22.3
	Dried 6 weeks	17.8	16.5	45.0	20.6

On one side of the constriction was introduced the mixture of platinum and carbon, and on the other side plugs of phosphorus pentoxide. Oxygen was passed through the tubes and the ends sealed. After leaving to dry for some time, the platinum-carbon mixture was heated to redness with no sign of visible combustion. Analysis of the residual gases in the tubes yielded the following results :—

(i) Dried for six weeks, heated to redness for three minutes,

CO₂—27 per cent., O₂—73 per cent.

(ii) Dried for three weeks, heated to redness for four minutes,

CO₂—34 per cent., O₂—66 per cent.

The amount of carbon burnt was about the same as when no platinum was present, but carbon dioxide only was formed. Carbon was also heated in dry oxygen in a platinum spiral to a bright red heat, but the glow disappeared directly the current was stopped. With a stronger current, the platinum was heated nearly to whiteness. The carbon showed visible combustion for two seconds, after which the glow died out. Analysis showed that over half the gas was still oxygen. In moist oxygen the combustion was rapid and complete on heating to dull redness. On heating carbon to dull redness in oxygen dried for a week, the residual gases were CO₂—5 per cent., CO—40 per cent., O₂—54.9 per cent., whilst in a tube which had been dried for two weeks the amounts were 2.2 per cent., 39.5 per cent., and 58.1 per cent. respectively. From this work Baker concluded that there were two stages in the combustion of carbon, firstly to

carbon monoxide, and thence, if conditions were favourable, to carbon dioxide.

In connection with the influence of water vapour on the combustion of carbon, it is interesting to note the effect of moisture on the products obtained by adsorbing and desorbing oxygen from a carbon surface. Reichardt¹ observed that the quantity of gas that could be expelled from carbon after the absorption of oxygen varied according to the degree of dryness. The subject was studied in much greater detail by C. J. Baker,² who found that if oxygen saturated with water vapour were allowed to "absorb" on charcoal, and the tube were then exhausted and kept at 100° C. for a week, a volume of carbon dioxide nearly seven times the volume of the carbon was evolved, but no carbon monoxide. If, however, either water vapour or dry oxygen were similarly absorbed, no gas was evolved. It was found that a temperature of 450° C. was required to remove the dried oxygen retained by the carbon, and carbon monoxide was the main product. The more free from moisture the substances employed were, the greater the yield of carbon monoxide proportional to carbon dioxide. When carbon dioxide was absorbed on carbon, the longer the drying the less the reduction to carbon monoxide. Hence he concluded that carbon is burnt directly to carbon monoxide by the absorbed and firmly retained oxygen.

Further investigations were carried out by Rhead and Wheeler.³ They baked carbon in an evacuated quartz bulb for forty-eight hours. Dry air was then admitted at the reaction temperature, and the residual gases pumped off. The temperature was raised to 1100° C. and the gases collected. There was little difference between the products in the "wet" and "dry" experiments. Hence they concluded that the formation of a compound C_xO_y (which they supposed to be produced on the adsorption of oxygen) was in no way prevented by drying the oxygen, but that moisture accelerated its decomposition.

Phosphorus and Oxygen.—As long ago as 1785, Bergmann observed that the spontaneous combustion of phosphorus occurred much less readily in the absence of moisture.⁴

"In vital air, without the aid of external heat, Phosphorus is consumed very slowly, and scarce at all, unless water be present to forward the decomposition by a double attraction."

¹ *J. pr. Chem.*, **98**, 418.

² *J. Chem. Soc.*, **51**, 249 (1887).

³ *Ibid.*, **103**, 1210 (1913).

⁴ *A Dissertation on Elective Attractions*, English Trans., 1785, p. 213.

A similar observation was made about thirty years later by William Higgins,¹ but he came to an entirely erroneous conclusion as to the cause of the combustion.

“When dry phosphorus is confined over mercury in perfectly dry oxygen gas, no union will take place in a common temperature, so that the slow combustion of phosphorus is promoted by the azote, which acts on it as a solvent.”

He does not appear to have tested the effect of either dry air or of moist oxygen, or he could not possibly have made this grave mistake. This is all the more surprising in that he had already found that moisture influenced several other reactions.

Baker² studied the effect of moisture on the combustion of phosphorus in much the same manner as he adopted in the case of carbon. When ordinary phosphorus was very carefully purified and dried over phosphorus pentoxide, the luminosity gradually disappeared; after a few days it did not reappear, no matter how the pressure was altered. The phosphorus was then melted in the tube, and still no luminosity appeared. When boiled, a faint glow appeared for an instant and then disappeared. On the introduction of a little water, however, bright luminosity at once flashed out, and, without heating, the phosphorus burnt with a vivid white flame.

In another series of experiments, pure amorphous phosphorus was sealed into tubes with phosphorus pentoxide. In six tubes which had been drying for from two to five weeks, no visible combustion could be observed, though the temperature was high enough to distil the phosphorus.

It was found by E. J. Russell³ that oxygen dried by means of phosphorus pentoxide took an hour to be absorbed by phosphorus, whereas that dried by means of sulphuric acid was absorbed in two or three minutes. This latter was considered to be the optimum water vapour concentration, for when much more moisture was present, the action, owing, he supposed, to the formation of a protective film on the surface of the phosphorus, was considerably retarded. There needs to be an excess of water present before any ozone or hydrogen peroxide is formed during the spontaneous oxidation of phosphorus.

Sulphur and Oxygen.—The combustion of sulphur is con-

¹ *Experiments and Observations on the Atomic Theory*, Dublin, 1814, p. 50 (footnote).

² *J. Chem. Soc.*, **47**, 349 (1885); *Phil. Trans.*, **179A**, 575 (1888); *Proc. Roy. Soc.*, **45**, 1 (1888).

³ *J. Chem. Soc.*, **83**, 1263 (1903).

siderably inhibited by intensive drying, if it is not stopped completely. Baker¹ investigated this subject by placing sulphur at one end of a tube filled with oxygen, phosphorus pentoxide being introduced at the other end to dry the gases. The tube was sealed and left to dry for five days. It was then heated side by side with a similar tube containing sulphur in moist oxygen. The sulphur began to melt at the same point in both tubes. Soon afterwards there was a sudden explosion in the moist tube and a few seconds later a small blue flame appeared on the surface of the dry sulphur. This continued for a short time and was then extinguished. Analysis showed free oxygen to be present in the dry tube but not in the moist tube.

A specimen of very carefully purified sulphur was treated in the same way. The moist sulphur burnt with a sudden flash, whilst the dry sulphur was distilled to and fro several times in the tube without visible combustion. Analysis showed only one-twelfth of the oxygen to have been converted into sulphur dioxide.

Arsenic and Oxygen.—Bergmann² showed that dry air had no action on arsenic at ordinary temperatures, whilst the same observation was made later by Bonsdorff.³

On the other hand, Baker⁴ was unable to detect any difference in the high temperature combustion of arsenic in moist oxygen and in oxygen which had been dried for one or two months.

Other Non-Metals and Oxygen.—Baker could also detect no difference in the rate of combustion of tellurium (dried for two and three weeks), selenium (dried for two weeks and two months), or of antimony (dried for six weeks and four months). Pure boron burnt in dry oxygen at the bright red heat of the blowpipe flame.

Oxygen and Cuprous Iodide.—According to Lean and Whatmough,⁵ dry air liberates iodine from cuprous iodide as readily as does moist air.

¹ *J. Chem. Soc.*, **47**, 349 (1885); *Phil. Trans.*, **179A**, 575 (1888); *Proc. Roy. Soc.*, **45**, 1 (1888).

² *Opuscula Chimica et Physica*, 1780.

³ *Ann. Phys. Chem.*, **41**, 293 (1837).

⁴ *Phil. Trans.*, **179A**, 575 (1888).

⁵ *J. Chem. Soc.*, **73**, 155 (1898).

CHAPTER X.

SOLID-GAS REACTIONS (*continued*).

THE ACTION OF ACIDIC GASES ON METALS, BASES, ETC.

Hydrogen Chloride and Sodium.—According to J. B. Cohen,¹ hydrogen chloride dried by means of sulphuric acid and phosphorus pentoxide does not attack sodium at all readily. It retains its metallic appearance for a few weeks in the dry gas, but in time it slowly assumes a dark grey colour, and after several months a deeper violet-grey colour.

Hydrogen Chloride and Aluminium.—Again according to Cohen,¹ aluminium is unacted upon by very dry hydrogen chloride.

Hydrogen Chloride and Lead.—It has never yet been shown that hydrogen chloride has no action whatever on lead when it is perfectly dry, but the reaction is certainly very much retarded by even comparatively rough drying of the gas. U. R. Evans² passed a current of hydrogen chloride, dried by bubbling through sulphuric acid, through two tubes containing lead standing over sulphuric acid and water respectively. The lead standing over the water began to darken at the bottom after ten minutes. In seventeen minutes the blue interference colours had given place to dull grey. The specimen over sulphuric acid began to show faint interference tints in places at this stage. Hence, although tarnish had not been prevented entirely by this rough method of drying, the velocity of its formation was very much reduced.

Hydrogen Chloride and Lime.—It was discovered by Higgins³ that "pure calcareous earth (lime) will have no effect on muriatic gas when both are perfectly dry; yet water, to which the gas has no chemical affinity, will condense it; in this state it will readily form an intimate union with the lime."

Hydrogen Chloride and Manganese Dioxide.—According⁴ to

¹ *Chem. News*, **54**, 305 (1886).

² *Trans. Faraday Soc.*, **19**, 201 (1923).

³ *Experiments and Observations on the Atomic Theory*, Dublin, 1814, p. 51.

Hughes,¹ hydrogen chloride gas acts on manganese dioxide whether moisture is excluded or not.

Hydrogen Chloride and Carbonates.—Perfectly dry hydrogen chloride gas appears to exert no action whatever on calcite and witherite. Hughes and Wilson² investigated this subject by passing the gas first over copper turnings, then through tubes containing pumice moistened with sulphuric acid, and finally through pumice and phosphorus pentoxide. The gas, thus purified and dried, was passed over a weighed quantity of Iceland Spar at 130° C. for an hour. Only 0.04 per cent. increase in weight was observed after this period, whereas moist hydrogen chloride occasioned an increase of 3 per cent. With witherite (barium carbonate), an increase of 0.08 per cent. was observed, as against 14.7 per cent. required for complete conversion into barium chloride.

Hydrogen Chloride and Silver Nitrate.—It was shown by Hughes³ that when dry hydrogen chloride gas was passed over dry silver nitrate either at ordinary temperatures or at 100° C., only about 1 per cent. of the theoretical change took place after two hours.

Hydrogen Sulphide and Silver.—The influence of moisture on the progress of the reaction between hydrogen sulphide and silver was studied very carefully by Cabell.⁴ The reactants were dried with different degrees of care, and it was found that as greater precautions were taken to ensure the dryness of the materials, the less readily did the reaction proceed.

Firstly, pure, clean silver was heated in a glass tube, hammered, and put into a thin bulb tube, where it was heated gently, and dry air was passed over it; the silver was then sealed in the bulb. Pure hydrogen sulphide was dried over two feet of calcium chloride, and four inches of phosphorus pentoxide, and was then passed through a tube containing, in the middle, the silver tube, and at each end three inches of phosphorus pentoxide. Protective tubes were also used at the exit. A slow current of hydrogen sulphide was passed for three hours and then the tube containing the silver was broken, the current continued for three-quarters of an hour, and then the tube containing the silver and gas were sealed off. In twelve hours the silver was slightly tarnished, but the phosphorus pentoxide showed some signs of moisture. In three weeks it was considerably tarnished.

In a second experiment, the silver was left rough, and glass

¹ *Phil. Mag.* (v.), **35**, 531 (1893).

³ *Ibid.*, **35**, 531 (1893).

² *Ibid.*, **34**, 117 (1892).

⁴ *Chem. News*, **50**, 208 (1884).

wool was used instead of cotton wool for confining the phosphorus pentoxide. In twelve hours the silver was quite dark and the phosphorus pentoxide quite moist.

Thirdly, the silver was hammered and polished. It was then put directly in the tube with the phosphorus pentoxide and heated gently in dry hydrogen for an hour. Sulphuretted hydrogen was passed for three hours and the tube sealed. After twenty-four hours the edges of the silver only were slightly tarnished. At 150°C . the whole surface was darkened, however.

In a fourth experiment, the tube was dried by aid of exhaustion and passage of dry hydrogen. After four months, the less polished edges of the silver were slightly acted upon, but the main surface was unchanged in appearance.

Hence Cabell concluded that in the absence of water vapour, silver did not decompose hydrogen sulphide at ordinary temperature.

Hydrogen Sulphide and Copper.—The influence of moisture on the action of hydrogen sulphide on copper is of a particular interest on account of its bearing on the mechanism of the atmospheric corrosion of copper. U. R. Evans¹ showed that water vapour exerts a very pronounced effect on this reaction. Hydrogen sulphide, dried by bubbling through sulphuric acid, was passed over specimens of copper standing over water and concentrated sulphuric acid respectively. The specimen over water soon lost its bright metallic lustre and became first a fine rose, then purple, and then steely-grey before the dry specimen showed any change at all. After an hour, the specimen over water was dark grey, whilst that suspended over sulphuric acid had arrived at the stage reached by the copper standing over water in a minute.

Another series of experiments on the same subject were carried out by Vernon.² He suspended three similar strips of copper in similar stoppered wash-bottles as follows: (a) over phosphorus pentoxide; (b) over phosphorus pentoxide and dry benzene; (c) over water. After standing to allow the first two strips to dry, a slow stream of hydrogen sulphide was passed through the tubes. After two minutes, no change was observed in the first specimen, whilst characteristic changes occurred in the second. The specimen over water behaved in a striking manner. For about half a minute no change was visible. Colour changes then began suddenly, and proceeded very rapidly. Within two minutes it had passed through a deep blue stage

¹ *Trans. Faraday Soc.*, **19**, 201 (1923).

² *Ibid.*, 898 (1924).

and become steely-grey. After three minutes, the dry specimen was practically unaltered, whilst that over benzene showed a whole range of colour changes. After three hours' exposure, the appearance of the dry specimen was much the same as that of the wet specimen after two minutes' exposure to the gas.

Hydrogen Sulphide and Alkaline Earth Oxides.—It was first found by Veley¹ that perfectly dry calcium oxide was unaltered by perfectly dry hydrogen sulphide. This was considered by him to be a remarkable fact, since if the reaction progressed even to an infinitesimal extent, the corresponding amount of water would be eliminated, and would cause the reaction to proceed to its final completion.

Similarly, after drying by passage over calcium chloride and phosphorus pentoxide, hydrogen sulphide has very little action on magnesium oxide.² The rate of increase of weight with water present was to the rate of increase of weight with the dry materials in the ratio 1200 : 3, and 1200 : 8 in different experiments at 15° C., and 1200 : 11 at 40° C. Hydrogen sulphide has also no action on barium oxide between 15° and 90° C. when dry; with ferric oxide a slight amount of reaction was found to occur.

Hydrogen Sulphide and Metallic Salts.—In drawing attention to the important part played by water in chemical reactions, Parnell showed in 1841 that whilst moist hydrogen sulphide reacted vigorously with papers impregnated with salts of lead, mercury, and copper, there was no reaction if the hydrogen sulphide were very carefully dried.³ He considered that the effect of water in permitting reaction between these compounds did not wholly depend on its dissolving either the gas or the salt, for the following reasons :—

- (a) This want of action was specific, occurring only with particular salts.
- (b) Water in a state of combination with the salt, in which condition it can exert no solvent power, is sufficient to restore the activity of the gas.
- (c) On moistening different dry salts with absolute alcohol, which dissolves six times its own volume of hydrogen sulphide, and then exposing to the gas, still no action ensued.

Consideration of the nature of the salts on which the action of sulphuretted hydrogen is restrained, led Parnell to the con-

¹ *J. Chem. Soc.*, **47**, 484 (1885).

² Hughes, *Phil. Mag.* (v.), **33**, 471 (1892).

³ *British Assoc. Report*, 1841, p. 51.

clusion that the function of the water in permitting action is to combine with the acid set free by the hydrogen sulphide immediately on its liberation. He compared the action of water in these reactions to that between sulphuric acid of various concentrations and metallic iron or zinc. The metals do not dissolve in the concentrated acid, just as dry lead sulphate does not react when exposed to dry hydrogen sulphide; if, however, water be added, reaction ensues in both cases; according to Parnell the water in the one case unites with the sulphate of zinc and in the other with the sulphuric acid. He realised, however, that this explanation would not apply to all cases, since there were some salts which were unacted upon by sulphuretted hydrogen when dry, of which the acid possessed only very little affinity for water. For these cases he considered that the insolubility of the sulphide was the controlling influence.

It was also found by Hughes¹ that there was no action between dry hydrogen sulphide and salts of lead, arsenic, tin, cadmium, bismuth, antimony, silver, copper, mercury, cobalt, etc. The salts were tested by soaking on filter paper and drying. The dry gas did not redden blue litmus paper. The suggestion offered by Hughes to explain this non-reactivity was that the hydrogen chloride and hydrogen sulphide should be considered, not as acids, but as the anhydrides of acids.

Sulphur Dioxide and Iron.—It was found by U. R. Evans² that various specimens of iron could be kept in sulphur dioxide dried by sulphuric acid for four days without suffering any change at all; in the presence of moisture, darkening was caused in two hours, whilst within four days a thick crust of corrosion deposit was formed.

Sulphur Dioxide and Alkaline Earth Oxides.—Birnbaum and Wittich³ found that dry barium oxide reacts only slowly with sulphur dioxide at 200° C., but much more readily at 230° C., forming barium sulphite, BaSO_3 . Strontium oxide absorbed the gas much less readily, combination beginning only at 220° C. Dry calcium oxide was less active still, and did not unite with sulphur dioxide below 400° C. In the case of magnesium oxide, absorption began at 326° C. On the other hand, Veley, who appears to have used a much more careful drying technique, found⁴ that reaction between dry lime and dry sulphur dioxide commenced slightly at 300° C., and absorption was fairly

¹ *Phil. Mag.* (v.), **33**, 471 (1892).

² *Trans. Faraday Soc.*, **19**, 201 (1923).

³ *Ber.*, **13**, 651 (1880).

⁴ *J. Chem. Soc.*, **63**, 821 (1893).

complete at 350°C . The absorptive power of the hydrate was found to be two hundred times as great as that of the pure oxide.

Sulphur Dioxide and Manganese Dioxide.—It was first shown by E. J. Russell and N. Smith¹ that the reaction between manganese dioxide and sulphur dioxide ceased when moisture was absent. Their drying was of a very careful type, being carried out in a similar form of apparatus to that employed in their investigation of the catalytic combination of sulphur dioxide and oxygen (Fig. 4). This was previously dried by heating in a large flame in a current of dry air, and the large bulb filled with sulphur dioxide, which was left to stand over distilled phosphorus pentoxide. The smaller compartment was filled with nitrogen, and contained the manganese dioxide and more phosphorus pentoxide. The stoppers were lubricated with phosphorus pentoxide, and coated on the outside with a mixture of beeswax and vaseline to keep out moisture. After fifteen days, the tap was opened, and after a further period of fifteen days no reaction whatever had occurred. Under these conditions, rapid absorption of the sulphur dioxide occurs with moist manganese dioxide.

Sulphur Trioxide and Calcium Oxide.—Pure dry sulphur trioxide vapour does not react with pure dry lime. This was first shown by Baker,² who prepared the lime in a pure state by igniting chalk mixed with sugar. This was introduced whilst warm into a small bulb blown on a hard glass tube, at the other end of which was placed some phosphorus pentoxide. The end of the tube containing the lime was heated at intervals to distil any moisture over to the pentoxide. After three days the portion containing the lime was sealed off. A glass tube was dried by drawing a current of dried air through it whilst it was heated nearly to its softening point. When cool, the bulb containing the dried lime was introduced at one end, and plugs of phosphorus pentoxide at the other; the tube was then exhausted, sealed off, and allowed to stand for two days, the part containing the bulb being heated at intervals to dry it as completely as possible. One end of the tube was connected by a joint of previously ignited asbestos to a tube containing sulphur trioxide, which was heated gently. The point of the evacuated tube was then broken by pressing against the side of the sulphur trioxide tube, and the sulphur trioxide drawn into the former. This was cooled by melting snow. When sufficient sulphur trioxide had been introduced, the end of the tube was again sealed, and the whole set

¹ *J. Chem. Soc.*, **77**, 346 (1900).

² *Ibid.*, **65**, 611 (1894).

aside for a week. The part of the tube containing the phosphorus pentoxide was then sealed off, and the bulb of lime broken. No sign of combination appeared. On allowing moist air to enter, however, the lime and sulphur trioxide combined with incandescence.

Sulphur Trioxide and Copper Oxide.—Using a similar technique to that employed in the case of lime, Baker was able to show that sulphur trioxide could be crystallised on dry cupric oxide without converting any of it into the white anhydrous copper sulphate.

Carbon Dioxide and Calcium Oxide.—As has been mentioned in an earlier chapter, it was first discovered by Bucquet in 1780 that it was necessary for water to be present in order that carbon dioxide might be absorbed by quicklime, and this, so far as the present author is aware, constitutes the first direct mention in the literature of the necessity of the presence of small traces of moisture for the progress of reactions not involving water in their simple equations.¹ On this account it may be of interest to give here a direct translation of this portion of Bucquet's address.

Two ounces of quicklime were taken, and after having reduced it to a powder, it was placed in a Macbride apparatus. After having evacuated the apparatus, it was filled with carbon dioxide generated from a mixture of sulphuric acid and "sel alkali de tartre." The lime was left in this gas for three days, and the carbon dioxide was renewed three times; at the end of this time the lime had not increased in weight. This was repeated several times. The lime which had been submitted to the action of the carbon dioxide in this way was compared with ordinary quicklime but no difference could be detected in the manner in which they behaved with respect to water and acids. Both decomposed sal ammoniac with equal facility without heating, and both yielded equal amounts of ammonia on distillation. Hence it was concluded that it was insufficient to expose lime to the action of carbon dioxide in order for it to pass into chalk, but that an intermediary was necessary in order that reaction might occur, and that this intermediary was water. ("D'ou je conclus qu'il ne suffit pas de rendre à la chaux de l'air fixé pour la convertir en craie, qu'il faut un intermède que cette union se fasse, et que cet intermède est de l'eau.")

On the other hand, it was soon discovered that anhydrous lime absorbs dry carbon dioxide at higher temperatures.

¹ J. B. M. Bucquet, *Mem. Acad.*, 9, 563 (1780).

Petzhold¹ found that this occurred when anhydrous lime was raised to a white heat in a current of the gas, whilst Rose² found that even at a red heat water-free lime combined considerably with carbon dioxide but did not quite form the saturated salt. An indication of the lower limit of the range of temperature over which dry lime absorbed dry carbon dioxide was given by Schultaschenko,³ who found that absorption did not occur at about 360° C. when the reactants were dry.

The same phenomenon was rediscovered later by Debray,⁴ who was apparently in total ignorance of the previous work. He concluded that quicklime does not absorb a trace of dry carbon dioxide at ordinary temperatures, combination not commencing until a red heat was attained.

Further experiments on this subject were described by Kolb,⁵ who, strangely enough, rediscovered the phenomenon in the same year as Debray. Kolb exposed finely powdered anhydrous lime to a current of perfectly dry carbon dioxide, which was renewed several times every day. After a month's treatment, the lime was unaltered in weight, and had absorbed no trace of gas. This result could be obtained consistently. Similar experiments with anhydrous magnesia and baryta gave the same result. The same procedure was repeated with calcium hydroxide, which was reduced to a fine powder and dried at 120° C. This also gained no weight in a month. Magnesium and barium hydroxides behaved in exactly the same manner. On the other hand, they all absorbed the gas when it had been passed through wash-bottles so as to moisten it. This was made more rapid still when the hydroxides were made pasty with water.

Kolb considered that there must be attributed to water either a mechanical action or a solvent action. He leant to the latter view, since he had shown that carbonisation was the slower the less the solubility of the hydroxide in water. Thus the rate was greater with baryta than with lime, which in turn was greater than that with magnesia. When in complete solution, the rates were found to be in the same order. When the hydroxides were only made pasty with water, the rates of reaction were proportional to the water added. It was immaterial whether the water were in the solid or in the gas.

As the result of a large number of experiments, Scheibler⁶

¹ *J. prakt. Chem. (i.)*, **17**, 464 (1839).

² *Ann. Phys. Chem.*, **86**, 280 (1852).

³ *Dingler's Poly. Journ.*, **205**, 335 (1872).

⁴ *Compt. rend.*, **64**, 603 (1867); *Z. Chem.*, 1867, 302.

⁵ *Compt. rend.*, **64**, 861 (1867).

⁶ *Ber.*, **19**, 1973, 2865 (1886).

also came to the conclusion that dry carbon dioxide did not combine with the anhydrous oxides of the alkaline earth metals, nor with the monohydrates (hydroxides) and with $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$. Above this water concentration, the solids were attacked, yielding basic carbonates. This was confirmed by Finkener,¹ who also found that dry carbon dioxide acted on dry strontium oxide dihydrate, $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}$ forming a basic carbonate.

The subject was investigated with rather more precision by Veley,² who confirmed the fact that carbon dioxide did not combine with dry lime to any extent below 350°C ., nor at ordinary temperatures even with incompletely hydrated lime. The gas was passed successively through a water wash-bottle, two sulphuric acid wash-bottles, 1300 mm. of pumice and phosphorus pentoxide in a tube in a zigzag shape, a weighed *U*-tube fitted with perforated stoppers and containing lime, a weighed tube containing phosphorus pentoxide, and finally a sulphuric acid wash-bottle. Only slight increases in weight were observed with anhydrous quicklime; even when 3 per cent. of water was added, very slight absorption was noted. With 11.21 per cent. of water, reaction was very incomplete, but once begun appeared to proceed to a slight degree. With the hydrate $\text{Ca}(\text{OH})_2$, the absorption of gas was at first more complete, and when the hydrate became moist by the water kept back, the combination increased till chemical change was nearly complete. With the hydrate and 10 per cent. of water, the absorption was rapid, showing the effect of free, as distinct from combined, water. A rise in temperature was found to increase the absorption both with the anhydrous and hydrated forms.

According to Rohland³ the immeasurably slow reaction between dried carbon dioxide and calcium hydroxide is greatly accelerated if only 1 per cent. of water be added.

Carbon Dioxide and Alkali Metal Hydroxides.—Kolb⁴ first found that "anhydrous" potash and soda did not gain in weight on exposure to perfectly dry carbon dioxide. Even potassium and sodium hydroxide which had been melted and cooled into a fine plate affording a large surface, and then rapidly removed from the action of moist air, did not absorb the gas.

Carbon Dioxide and Silver Oxide.—When silver carbonate is heated in a tube containing phosphorus pentoxide, it gives a definite dissociation pressure on approaching equilibrium from the lower side, but the action appeared to Colson⁵ to be

¹ *Ber.*, **19**, 2958 (1886).

² *J. Chem. Soc.*, **63**, 821 (1893).

³ *Chem. Zeitung*, **30**, 808 (1906).

⁴ *Loc. cit.*

⁵ *Compt. rend.*, **132**, 467 (1901).

irreversible, the carbon dioxide not being absorbed by the silver oxide. He thought, however, that when due allowance had been made for the pressure of the water vapour, the dissociation pressures were about the same as in the "moist" case.

Carbon Dioxide and Lead Oxide.—In this case the rate of dissociation of the solid lead carbonate is greatly hindered by the absence of water vapour; when equilibrium was attained in six or seven hours in the case of the moist carbonate, ten or twelve times as long was taken in the case of a specimen which had been standing in contact with phosphorus pentoxide.¹ The carbon dioxide and lead oxide combined again only slowly in the "dry" case. This was explained by Colson as due to polymerisation due to the high temperature. He supposed that the principal factor governing the whole equilibrium $\text{PbCO}_3 \rightleftharpoons \text{PbO} + \text{CO}_2$, whatever it may be, is dependent on the partial pressure of water vapour present. Hence he supposed that this would be a general phenomenon for all dissociation and recombination reactions.

¹ Colson, *Compt. rend.*, **140**, 865 (1905).

CHAPTER XI.

SOLID-GAS REACTIONS (*continued*).

THE REDUCTION OF SOLIDS.

THE very wide class of reactions involving the action of reducing gases, such as hydrogen or carbon monoxide, on solid compounds, should furnish some very interesting examples of reactions for the progress of which small quantities of water are essential. Reactions in which hydrogen is the reducing agent should be of especial interest, since water is produced in these cases as one of the products of the reaction, and very careful drying indeed should be necessary in order to stop the reaction from commencing. Very few of these reactions have been investigated, however, and these have yielded very conflicting results. Hence no generalisations can be made at present.

Oxides of Iron and Hydrogen.—It would appear from some early work that moisture exerts a considerable influence on the reduction of oxides of iron by means of hydrogen, but the subject does not seem to have been followed up at all by recent investigators. Muller-Erbach¹ found that hydrogen reduced ferric oxide much less readily when the reactants were dry. In the case of the oxide obtained by heating the metal in air, the first sign of reduction, in the case of the dry materials, occurred at 330°, as against 293° when moist. With the oxide obtained by precipitation these values were 300° and 283° C. Throughout the work on the reduction of ferric oxide by hydrogen, slight discrepancies were obtained in the experimental results, which could be attributed to differences in the degree of drying in different cases.

In a later series of experiments² the same author found that when hæmatite was heated in sealed tubes with calcium chloride and hydrogen for seven, seventeen, and thirty-seven hours respectively, one-half, one-third, and one-eighth of the hydrogen remained. This he explained by supposing that the amount of

¹ *Ann. Phys. Chem.*, **136**, 53 (1869). ² *Ber.*, **18**, 3239 (1885).

moisture in the tube gradually decreased and consequently the reduction was retarded.

Copper Oxide and Carbon Monoxide.—The influence of moisture on the reduction of copper oxide by carbon monoxide has been investigated in detail by Purcell.¹ Pure copper oxide was powdered and dried in an apparatus of the type shown in Fig. 6, where it could be heated to 450° C. *in vacuo* whilst connected to a cooled bulb containing phosphorus pentoxide. When dry, the bulbs were drawn off, each containing about 0.2 gram of copper oxide. These were sealed into tubes of the form shown in Fig. 7, which could be filled with carbon monoxide. Phosphorus pentoxide was introduced into C, which was sealed off again. The tube was baked *in vacuo*, washed out with carbon

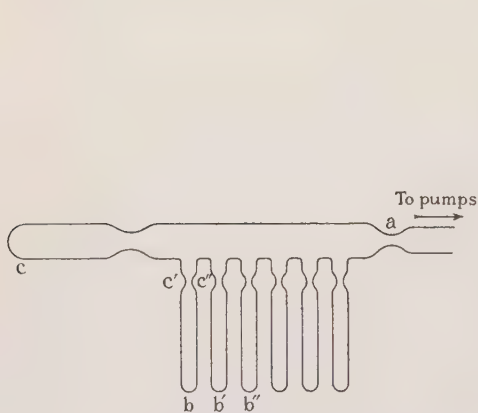


FIG. 6.

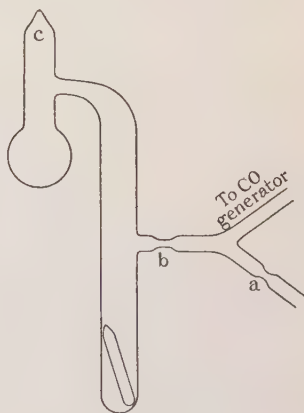


FIG. 7.

monoxide, and re-evacuated. The tube was finally filled with carbon monoxide at 60 cm. pressure, and sealed off. It was heated to 400° C. whilst the phosphorus pentoxide compartment was cooled. To examine a tube, the bulb of oxide was broken by dropping on the bottom of the tube. Reduction was followed by observation of the change of colour of the oxide, and since the carbon monoxide was always in excess, the product was always a mass of red copper.

In tubes from which the phosphorus pentoxide had been omitted, the copper oxide was completely reduced by heating at 100° C. for ninety minutes or at 150° C. for ten minutes. The temperature required for reduction increased with time of

¹ J. Chem. Soc., 1928, 1207.

drying, till a maximum was reached. The data obtained is given in Table XIV.

TABLE XIV.

Time of Drying.		Temp.	Time.
CuO.	CO.	°C.	
Nil	Nil	100	1½ hours
do.	do.	150	10 minutes
10 days	7 days	100	20 hours
do.	do.	180	90 minutes
1 month	1 month	425	15 minutes
6 months	18 months	425	?

Possible explanations offered by Purcell to account for this behaviour were (a) the oxides may react with carbon monoxide at 430° in the absence of water; (b) appreciable amounts of water are given off by the glass or cupric oxide at that temperature; (c) the dry carbon monoxide may be decomposed into carbon dioxide and carbon on the surface of the copper oxide, since carbon monoxide is known to be decomposed on catalytic surfaces at much lower temperatures.¹

Further information concerning the speed of this reaction was obtained by passing a stream of dry carbon monoxide over dry copper oxide and analysing the gas in 10 c.c. samples. The carbon monoxide was stored over concentrated sulphuric acid, and the gas from this reservoir displaced that from a large flask where it had been dried over phosphorus pentoxide, which again displaced the gas in second and third bulbs. It was passed over a gram of copper oxide in a boat heated in an electric furnace. The copper oxide was dried *in situ* by heating to 400° in a vacuum with a phosphorus pentoxide tube attached.

If the copper oxide were not intensively dried, a normal reduction curve was observed; viz. (a) a short induction period; (b) a period of reduction at a regular rate; (c) a decrease as all the copper oxide becomes reduced. When the reactants were dried, the amount of carbon dioxide formed was much reduced, and it did not become greater with time. Table XV. shows the amounts of carbon dioxide found in the issuing gas at the given time, the reactants having been dried for seven days. Table XVI. shows the normal reduction.

¹ Cleminson and Briscoe, *J. Chem. Soc.*, 1926, 2148.

TABLE XV.

Temperature of Oxide, 150° C.

Time (minutes) . . .	90	120	150	195	240	270
CO ₂ per cent. . . .	0.5	0.5	0.4	0.6	0.4	0.4

Temperature increased to 196° C.

Time (minutes) . . .	330	350	360	371	410	480
CO ₂ per cent. . . .	4.4	4.4	5.0	5.5	5.6	5.5

TABLE XVI.

Temperature of Oxide, 150° C. (Undried).

Time (minutes) . . .	9	15	30	42	60	87	101
CO ₂ per cent. . . .	0.1	0.5	1.4	3.0	9.0	17.0	25.0

Table XVII. gives the constant percentages of carbon dioxide obtained in comparative experiments at different temperatures. The period of drying in each case was one week.

TABLE XVII.

CO ₂ per cent.	0.4	0.6	3.0	5.0
Temperature of CuO . .	150	160	180	195

Thus the speed of the reduction depends on the temperature and on the amount of water present. The copper formed does not appear to catalyse the reaction when only a very little water is present, although it does so when the system has not been dried.¹

These experiments were extended by investigation of the influence of a dry third substance on the reduction. Sulphur dioxide, bromine, ether, alcohol, and benzene were dried in an apparatus of the form shown in Fig. 8. Pure phosphorus pentoxide was placed in *a*, and some was sublimed in dry oxygen into each of the small bulbs. A small quantity of one of the liquids was placed in the flask and the neck sealed off. The apparatus was evacuated whilst the liquid was cooled. After sealing at *c*, the bulbs were sealed off at the constrictions (*b*, *b'*) so as to contain about 2 c.c. of vapour. With sulphur dioxide, the gas was introduced so as to contain about 1 c.c. at N.T.P. After drying for two months, the bulbs were sealed into outer tubes (Fig. 9), copper oxide being placed in the other limb. The tubes were cleaned and filled with carbon monoxide, the phosphorus pentoxide being placed with the third substance. After drying, the tubes were broken by a weight *K*, and the copper oxide bulb by shaking. The copper oxide was heated to 110° for twenty-four hours without reduction; there was no change in six hours

¹ Jones and Taylor, *J. Physical Chem.*, **27**, 623 (1923).

at 175° in any case; but in half an hour at 225° the oxide in the alcohol, ether, and benzene tubes was reduced. The sulphur dioxide and bromine tubes were unchanged in half an hour at 275° , 325° , and 375° C., but at 425° the oxide was reduced in each case. Thus the organic vapours seemed to catalyse the reaction, but not so efficiently as water. Two possibilities were suggested by Purcell; (a) the liquids may begin to undergo incipient decomposition with the copper oxide; or (b) they may have been insufficiently dried.

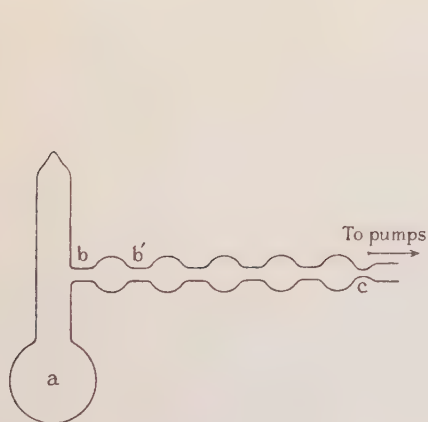


FIG. 8.

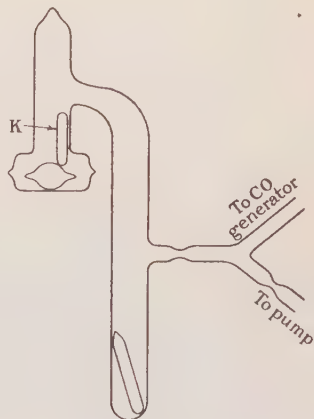


FIG. 9.

Bismuth Oxide and Carbon Monoxide.—The reduction of bismuth oxide by means of carbon monoxide was investigated by Purcell¹ in an analogous manner to the case of cupric oxide. It was found that the readiness of reduction of bismuth oxide by carbon monoxide decreased with increasing period of drying; thus with the undried material reduction was complete in two and a half hours at 175° C. and in a few minutes at 250° , but after drying the reactants for ten weeks, a temperature of 430° was required for reduction to occur.

Mercuric Oxide and Carbon Monoxide.—In opposition to the results obtained with copper and bismuth oxides, Purcell found that the reduction of mercuric oxide was rapid at 180° C. when undried, and that drying of both the mercuric oxide and the carbon monoxide for from eight months to a year produced no difference whatever in this rate.

¹ *Loc. cit.*

Silver Oxide and Carbon Monoxide.—In an exactly similar manner, Purcell showed that silver oxide was reduced within thirty minutes at room temperature. Attempts were made to dry the oxide by keeping it for as long as eighteen months at 15° , 100° , or 200° , the bulbs then being sealed into outer tubes in which the carbon monoxide was dried for as much as six months, but no change was observed in the rate of reduction.

Copper Oxide and Hydrogen.—This system was also investigated by Purcell. The copper oxide was dried as in the

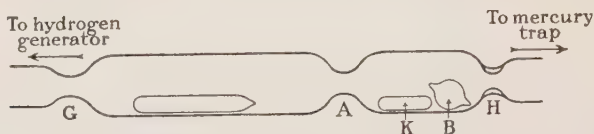


FIG. 10.

case of the carbon monoxide-copper oxide investigation, and introduced into tubes as in Fig. 10. Pure hydrogen was passed through the heated apparatus for four hours. The tube was sealed off while warm at the capillaries *G* and *H*, so the gas was under slightly reduced pressure on cooling. The phosphorus pentoxide bulb *B* was broken by breaker *K* and the compartment containing the copper oxide bulb kept at 400° . When a tube was thought to be dry, it was sealed at *A*, and the copper oxide bulb broken. With periods of drying up to two years no differences were observed between wet and dry materials.

CHAPTER XII.

SOLID-GAS REACTIONS (*continued*).

OTHER REACTIONS BETWEEN SOLID AND GASEOUS PHASES.

Chlorine and Metals.—The fact that moisture exerts a very pronounced effect on the readiness with which the halogens attack metals appears to have been first recorded by Andrews.¹ His opinions are best given in his own words:—

“The description generally given in chemical works of the rapid manner in which zinc, copper, antimony, etc., enter into combination with chlorine gas at ordinary temperatures is only true when the gas is in a moist state. Chlorine gas, when carefully dried, has no action whatever, at the ordinary temperature of the atmosphere, upon fine filings of zinc or iron, or upon copper reduced from its oxide by means of hydrogen gas, although the action, as is well known, is most energetic if moisture be present. On the contrary, the dry gas instantly combines with arsenic, antimony, and phosphorus. This striking difference appears to depend upon the circumstance that the compounds formed by chlorine with the former substances are solid at common temperatures and very fixed, while those formed with antimony and arsenic are fluid and volatile. The chloride of phosphorus is also very volatile. If, however, the chemical affinity be very intense, combination will take place. Thus potassium inflames in dry chlorine gas, but the chloride which is formed terminates the action before the whole of the metal has entered into combination. The fluidity of the metal also exercises an important influence in determining the combination—as in the case of mercury, which slowly combines with dry chlorine. The preceding remarks may also be applied to the behaviour of dry bromine when brought into contact with metals.”

Similar effects were observed in the case of the union of chlorine with sodium by Wanklyn,² but he does not appear to have

¹ *Trans. Royal Irish Academy*, **19**, 393 (footnote), (1842), *Scient. Memoirs*, 1889, p. 90.

² *Chem. News*, **20**, 271 (1869).

realised that it was the absence of moisture which caused the effect he observed. He stated that

“ When chlorine gas is passed over metallic sodium, even when the metal is fused and whilst in a state of fusion shaken in contact with the gas so as to expose a fresh metallic surface, there is no action. A glass vessel containing a piece of sodium was weighed ; and, after the transmission of chlorine under the circumstances above-named it was re-weighed.

	Grams.
Weight before the action of chlorine .	7·847
Weight after the action of chlorine .	7·863
	<hr/>
Gain . . .	0·016

The quantity of metallic sodium taken for the experiment was 0·770 gram.”

Some years later it was noticed by Cowper¹ that sodium tarnished very slowly in chlorine rather drier than usual ; and he anticipated that when very dry it might not react at all. At that time he had not observed Wanklyn's note. Cowper washed chlorine free from hydrogen chloride in three wash-bottles, and then passed it through eight feet of calcium chloride. This gas reacted very slowly on Dutch Metal. A minute quantity of water caused reaction to proceed. A drop of water placed on the metal caused rapid reaction with evolution of heat. With zinc, a slight amount of moisture was observed to collect on the metal towards the inlet tube. Hence he suggested that zinc foil might prove a good means of removing the last traces of water from chlorine. He adopted this method in his later experiments. Of course, the dampness he observed was doubtless due to the formation of a little of the very hygroscopic zinc chloride near the point where the gas entered. The drying power of this zinc chloride appears to have been quite good enough to prevent the combination of the chlorine with the zinc further into the reaction vessel. Cowper found that chlorine which had been dried for some days over calcium chloride did not attack zinc ; magnesium wire was also unattacked, but silver was slowly attacked, bismuth was slightly tarnished, and tin foil readily acted upon. Arsenic and antimony powders were acted upon immediately, with evolution of heat and light. He noted that the last three gave liquid chlorides, and considered that this fact in some way influenced the combination of these elements. Thus he came to

¹ *J. Chem. Soc.*, **43**, 153 (1883).

the same conclusion in this respect as Andrews, although he appears to have been quite in ignorance of the latter investigator's work.

Dixon and Harker¹ observed that pieces of lead sealed in dry chlorine were not much acted on, the colour of the gas being visible after some weeks.

Very similar results to those of Cowper were obtained later by Kreusler,² who also seems to have been quite unaware of any previous work on the subject. He found that dry chlorine did not attack "falsche Gelb," brass, and other metals when dry, but that addition of a drop of water caused reaction to occur. Antimony powder was found to react even in the dry gas; he attributed this either to the possibility that moisture was not necessary for the progress of this reaction, or that the antimony powder still held a little moisture on its surface.

According to Shenstone³ dry chlorine, bromine, and iodine all acted upon mercury as readily in the dry state as when moist.

Confirmation of this in the case of chlorine has been obtained by Germann,⁴ who used the novel plan of drying his apparatus with phosgene. Since phosgene readily hydrolyses in the presence of moisture, yielding hydrogen chloride and carbon dioxide, he assumed that small amounts of moisture should be rapidly decomposed by phosgene, especially at an elevated temperature. In an effort to dry his materials with phosgene, he partially filled a tube with liquid phosgene and left it for some time at room temperature. He then allowed the phosgene to boil away, and heated the tube with a free flame, at the same time evacuating it; after several repetitions of this process he distilled several grams of pure mercury into the tube from a side tube which had also been subjected to the phosgene and heat treatment. A solution of chlorine in phosgene, which had been standing for several days at room temperature, was then distilled into the mercury, but the latter reacted immediately and completely with the chlorine. Germann considered that it was improbable that this result was to be explained by the phosgene playing the rôle of water in catalysing this reaction, because Klein found⁵ that the reaction between hydrogen sulphide and sulphur dioxide is not influenced by the presence of halogen derivatives, and also a solution of chlorine in liquid phosgene does not attack magnesium.

¹ *Mem. Manchester Lit. and Phil. Soc.* (iv.), **4**, 3 (1890).

² *Ber.*, **24**, 3947 (1891).

³ *J. Chem. Soc.*, **71**, 471 (1897).

⁴ *J. Physical Chem.*, **28**, 1218 (1924).

⁵ *Ibid.*, **15**, 1 (1911).

Another curious observation, made by Baker, is that dry chlorine attacks platinum in light but not in darkness.¹

The Action of Chlorine on Lime.—The fact that lime does not absorb dry chlorine, but does so when moisture is present, appears to have been first mentioned by Gilbert,² and since that time has been rediscovered and investigated by many different chemists, many of whom have come to rather conflicting conclusions on the subject. Thus Weiss³ considered that chlorine acted on dry slaked lime only under the action of light, whilst Morin⁴ considered that quicklime with half a molecular weight of water added absorbed a quarter of an atomic weight of chlorine, and with one to two molecules of water absorbed one to two atoms of chlorine.

Again, Horton Labillardiere⁵ said that if lime were slaked and then dried by heating to 100° C., 47 parts of the dried lime absorbed 53 parts by weight of chlorine. On the other hand, Graham⁶ found that whilst slaked lime which had been dried over sulphuric acid absorbed chlorine very readily, that which had been dried at 100° C. did not absorb any at all. This last observation was also confirmed by Bollen.⁷

The subject was investigated in somewhat greater detail by Tchingianjanz, Fricke, and Reimer,⁸ who repeated Graham's experiments very carefully. They found that calcium hydroxide which had been dried on a water bath and then exposed to the action of dry chlorine only increased in weight by 0.98 per cent. in an hour and a half. On the other hand, lime which had been dried by standing over sulphuric acid absorbed 29.9 per cent. of its weight of chlorine in the same time. The excess of water present in the case of the lime dried over sulphuric acid above that remaining when drying was carried out over a water bath was found to be equal to 0.402 per cent. of the weight of the lime. This was considered to be a very small amount to produce such a change in the velocity of the reaction. It was found that absorption occurred much more readily at higher temperatures.

Similar observations were made at a much later date by Veley,⁹ who appears to have been totally unaware of the previous work.

¹ Private communication to Mellor, *vide J. Chem. Soc.*, **81**, 1291 (1902).

² Gilbert's *Ann.*, **49**, 315 (1815).

³ See Tchingianjanz, Fricke, and Reimer, *Dingler's Jour.*, **192**, 297 (1869).

⁴ *Ann. Chim. Phys.* (ii.), **37**, 139 (1828).

⁵ *J. Chem. Med.*, **1**, 501 (1825).

⁶ See Tchingianjanz, Fricke, and Reimer, *loc. cit.*

⁷ *Ibid.*

⁸ *Loc. cit.*

⁹ *J. Chem. Soc.*, **65**, 1 (1894).

He stated that dry lime does not combine with dry chlorine at ordinary temperatures to form the so-called bleaching powder. No appreciable change was observable below 300°C ., when partial replacement of oxygen by chlorine took place.

The lime, after ignition in a platinum crucible, was placed in a piece of hard combustion tubing, sealed at the lower end and with a constriction at the upper end; the latter was partially closed with asbestos fibre, beyond which a plug of phosphorus pentoxide was placed. The tube up to the constriction was heated for some hours in a combustion furnace, allowed to cool slightly, and cut off at the constriction. The hot lime was poured into a *U*-tube, which had been baked in a nitre bath for some time. Before being admitted to this *U*-tube the chlorine gas was passed for some hours through a system of water and sulphuric acid bottles and phosphorus pentoxide tubes, set up as in the case of Velej's work on the absorption of sulphur dioxide and carbon dioxide by lime, so as to diminish the risk of any reaction occurring yielding hydrogen chloride.

Winteler¹ also found that when calcium hydroxide was heated in a drying oven at 120°C ., and then exposed to the action of dry chlorine, no action occurred, but that the introduction of a small amount of moisture caused vigorous reaction, with evolution of heat.

The Action of Chlorine on Potassium Iodide and Potassium Bromide.—It was found by Parsons² that dry chlorine had no appreciable effect on the weight of potassium iodide at room temperature (20° to 24°C .) even after the chlorine had been passed over it for more than an hour. The only evidence of even a slight reaction was that the iodide turned a pale straw colour. Table XVIII. shows the effect of various concentrations of water vapour in the chlorine on the extent of the conversion. In each case the chlorine was passed for an hour at the rate of 100 bubbles per minute at a temperature of 20° to 24°C .

TABLE XVIII.

P.p. of Water Vapour (mm.).	Conversion of Iodide, per cent.
0.0	0.04
4.2	0.4
7.3	1.7
10.0	3.6
14.2	5.6
23.5	10.7

¹ *Z. anorg. Chem.*, **33**, 161 (1902).

² *J. Amer. Chem. Soc.*, **47**, 1817 (1925).

The purified iodide was dried at 120° C. and then powdered whilst hot. It was kept in a desiccator over phosphorus pentoxide till used. The chlorine was dried by two towers of sulphuric acid and then by four tubes of phosphorus pentoxide. The extent to which the reaction had proceeded was measured by obtaining the loss in weight of the well-dried halide, after the iodine set free by the chlorine had been removed by evacuation and heating to 200° to 250° C. in a current of dry air. The partial pressure of water in the chlorine for amounts up to 10 mm. was controlled by bubbling the gas through saturators containing various concentrations of sulphuric acid at suitable temperatures. For higher partial pressures, the gas was passed through water.

Similar results were obtained with potassium bromide.

TABLE XIX.

Temp. (°C.),	P.p. of Water Vapour (mm.).	Conversion of Bromide, per cent.
20	6.0	0.5
	10.1	1.6
	12.0	12.5
	14.2	14.5
	17.4	20.3
30	14.2	0.5
	19.6	1.7
	22.1	9.6
	25.0	11.5

Thus it was concluded that there is a minimum effective concentration of water vapour before any considerable reaction takes place. The sudden increases at 12.0 and 22.1 mm. respectively coincide with the partial water vapour pressure of the saturated salt solutions. Hence the results were explained on the assumption that the reaction really takes place only in solution.

The Action of a Mixture of Hydrogen Sulphide and Carbon Disulphide on Titanium Sesquioxide.—It is stated by Thorpe¹ that when a steady stream of hydrogen sulphide, carefully dried by passage through sulphuric acid, is passed through carbon disulphide and the vapours then passed over titanium sesquioxide heated to redness, no reaction occurs, although when the gas is not dried titanium sesquisulphide is readily formed.

Ammonia and Mercurous Chloride.—Jatindranâth Sen² showed that ammonia which had been dried, but not Bakerian dried, had only a slight action on mercurous chloride.

¹ *J. Chem. Soc.*, **47**, 492 (1885).

² *Z. anorgan. Chem.*, **33**, 204 (1903).

CHAPTER XIII.

REACTIONS BETWEEN SOLIDS.

THE influence of moisture on the progress of reactions in which two solid phases are concerned is by no means fully understood, and it is very uncertain whether the effect can be compared with the influence of water on reactions between, say, solid and gaseous phases, or not. Hence a brief résumé only is given here of the more important experiments which have been carried out on the influence of water vapour on such reactions.

Calcium Oxide and Ammonium Chloride.—It was shown by Baker¹ that dry lime had no action on dry ammonium chloride. The ammonium chloride was purified by boiling the sublimed chloride with dilute nitric acid, and then with water. The crystallised product was dissolved and recrystallised eight times. It was sublimed in a hard glass tube, and while still hot was placed in the middle of a hard glass tube in which there were two constrictions; into one end of this tube, which had been previously heated to redness in dry air, lime was introduced, phosphorus pentoxide being placed in the other. One end was drawn out into a conducting tube, while the other was sealed. After seventeen days, with gentle heating, the end of the conducting tube was broken under dried mercury, and part of the ammonium chloride shaken into the lime. About 9 c.c. of gas were collected but it had no smell of ammonia. The conducting tube was then withdrawn from the mercury, and moist air allowed to enter the tube as it cooled. The rest of the ammonium chloride was then mixed with the lime and heated, when ammonia was evolved.

Balarev's Investigations.—The influence of moisture on a large series of reactions between solid phases has also been studied by Balarev,² who considers that no reactions can actually occur in the solid state and that in cases where this appears to occur,

¹ *J. Chem. Soc.*, **65**, 611 (1894).

² *Z. anorgan. Chem.*, **134**, 117 (1924); **136**, 216 (1924); **138**, 349 (1924); **143**, 89 (1925); **145**, 121 (1925).

one of the reactants is melted superficially. The greater reactivity attributed by Hedvall and Heuberger¹ to solids in the neighbourhood of their transition temperatures he ascribed to the presence of fused or liquefied layers. On the other hand, Hedvall and Heuberger consider that reaction does actually occur between solids which have been dried carefully, although the presence of water may lower slightly the temperature at which the reaction begins and also facilitates its progress.² They reject completely Balarev's surface fusion theory.

Calcium Oxide and Silicon Dioxide.—Balarev finds that the tension of water vapour in the system calcium oxide—silicon dioxide determines not only the velocity of the reaction between the oxides, but also the initial temperature at which the reaction proceeds with a measurable velocity. A mixture containing equivalent proportions of the two oxides, when heated at 920° C. in a stream of hydrogen saturated with water vapour at 95° C. showed 46 per cent. of combined calcium oxide after a period of 150 minutes. Even at this temperature, absorption of water occurred, and although no definite compound was formed, some of the chemical properties of a hydrate were found to exist. Although the accelerating influence of water was the greatest, the presence of other gases also influenced the velocity. Traces of hydrogen chloride and hydrogen sulphide greatly accelerated the reaction, owing, Balarev considered, to the formation of fusible surface films. In the other cases investigated, Balarev supposed that the gas was adsorbed, and that the adsorbed layer caused a loosening of the surface layer of molecules, an effect which was comparable with the softening or melting.

Reactions between calcium oxide and other solids above the temperature of dissociation of calcium hydrate were found to be comparatively slow unless the other solid caused the formation of a fused or liquid layer, as in the cases of molybdenum trioxide, tungstic oxide and silver pyrophosphate.

Sodium Sulphate and Barium Carbonate.—In the reaction between sodium sulphate and barium carbonate no detectable reaction takes place at 430° C. when these substances are dried carefully, whilst in the presence of water vapour Balarev found that double decomposition became rapidly possible.

Barium Oxide and Acidic Oxides.—Barium oxide combines vigorously with lead dioxide, manganese dioxide, and U_3O_8 at temperatures below 360° C., with evolution of much heat. The temperature at which the reaction begins depends on the water

¹ *Z. anorgan. Chem.*, **135**, 49 (1924).

² *Ibid.*, **140**, 243 (1924).

content of the mixture and on the pressure to which the mixture has been subjected; an increase in either causes a lowering of the reaction temperature. A mixture of barium oxide and stannic oxide, whether compressed or not, was found not to react below 360°C ., the melting-point of barium hydroxide, and little heat is evolved in the reaction. In all these reactions, the presence of a small amount of barium hydroxide acts as a catalyst in accelerating the combination of the two oxides, and it was assumed by Balarev that this was due to the formation of a film of liquid or nearly liquid hydroxide on the particles of barium oxide. When the two oxides were pressed strongly together, the heat generated by slight local action was supposed to be sufficient to melt the hydroxide, and that reaction then set in with increasing vigour to completion. His theory was also supported by the observation that barium oxide containing a trace of water reacted with manganese dioxide at 240°C ., whilst calcium oxide did not do so below 930°C .

Barium Oxide and Calcium Carbonate.—It was found by Balarev that barium oxide and calcium carbonate reacted to the extent of 90 per cent. in the presence of even a trace of water. This was attributed to the continuous formation of barium hydroxide by dehydration of the calcium hydroxide produced in the reaction. It was assumed that the reaction took place only between the barium hydroxide and the calcium carbonate, and hence that the velocity was determined by the velocity of the diffusion of water from the place at which the reaction was already complete to the barium oxide.

Potassium Chlorate and Manganese Dioxide.—The rôle of water in the catalytic decomposition of potassium chlorate by means of manganese dioxide was supposed by Balarev to be similar to that in the other cases, except that the potassium chlorate, or the system potassium chlorate—potassium chloride softens, and as such was catalysed by the manganese dioxide. It was found that a moist mixture of manganese dioxide and potassium chlorate reacted at a temperature 12° lower than it did when dried carefully.

CHAPTER XIV.

REACTIONS IN NON-AQUEOUS SOLVENTS.

It is felt that no work on this subject would be complete without some reference to the influence of moisture on reactions in solvents other than water, but the nature of this influence is of an extremely complicated nature. It does not appear to be due entirely to the necessity of the presence of an ionising solvent, although this factor doubtless plays an important rôle in certain cases, because certain metals will dissolve quite well in a non-conducting solution of hydrogen chloride in an anhydrous solvent. In many cases the solubility of the product in the solvent in question appears to be the controlling influence. Such cases really fall outside the scope of this subject, but it is extremely difficult to differentiate between the different classes.

Hydrogen Chloride and Metals.—It was observed by Gomburg¹ that zinc was acted on by a solution of dry hydrogen chloride in dry ethyl acetate, although this latter solution did not conduct electricity. Similarly, Kahlenberg² prepared a solution of hydrogen chloride in benzene which was no better conductor than the dry benzene itself. This solution did not attack bright magnesium ribbon, iron, nickel, copper, cadmium, mercury, or silver, nor, of course, gold and platinum. On the other hand, zinc was readily acted on, hydrogen being evolved. Platinum foil in contact with the zinc had no effect on the reaction, the hydrogen being evolved from the zinc only. In the same way, platinum did not cause the magnesium to decompose the acid. Tin and aluminium were slightly acted upon, and lead very slightly. Metallic sodium was fairly rapidly acted on. In most cases, the chlorides, being insoluble in benzene, formed a protective coating over the metal.

A detailed study of the action upon metals of solutions of hydrogen chloride in various non-aqueous solvents was made by H. E. Patten.³ The results he obtained may be summarised as

¹ *Amer. Chem. Jour.*, **25**, 324 (1901).

² *J. Physical Chem.*, **6**, 1 (1902).

³ *Ibid.*, **7**, 153 (1903).

follows. Magnesium was more or less acted upon by dry solutions of hydrogen chloride in chloroform and ethyl chloride, and was corroded after two hours in carbon tetrachloride. It was unattacked in benzene, silicon tetrachloride, stannic chloride, phosphorus trichloride, or antimony pentachloride. Aluminium was attacked in chloroform, carbon tetrachloride, ethyl chloride, and sulphur monochloride, but not in benzene, silicon tetrachloride, stannic chloride, phosphorus trichloride, and antimony pentachloride. Chromium was attacked in chloroform and ethyl chloride, but not in stannic chloride, antimony pentachloride, sulphur monochloride, or thionyl chloride. Manganese was attacked in chloroform and ethyl chloride, but not in stannic chloride, antimony pentachloride, sulphur monochloride, or thionyl chloride. Zinc was attacked in chloroform, carbon tetrachloride, ethyl chloride, benzene, sulphur monochloride, and thionyl chloride, but not in silicon tetrachloride, stannic chloride, phosphorus trichloride, or antimony pentachloride. Iron was attacked in carbon tetrachloride, ethyl chloride, and sulphur monochloride, but not in chloroform, silicon tetrachloride, or stannic chloride. Cobalt was attacked in ethyl chloride, but not in silicon tetrachloride, phosphorus trichloride, or antimony pentachloride. Nickel was attacked in chloroform, and in arsenic trichloride, but not in carbon tetrachloride, ethyl chloride, silicon tetrachloride, stannic chloride, phosphorus trichloride, antimony pentachloride, sulphur monochloride, or sulphuryl chloride. Lead was attacked in chloroform, carbon tetrachloride, ethyl chloride, silicon tetrachloride, phosphorus trichloride, antimony pentachloride, and sulphur monochloride, but not in stannic chloride. Cadmium was attacked in chloroform, carbon tetrachloride, ethyl chloride, and benzene, but not in silicon tetrachloride, stannic chloride, phosphorus trichloride, antimony pentachloride, sulphur monochloride, or thionyl chloride. Tin was attacked in chloroform, carbon tetrachloride, ethyl chloride, phosphorus trichloride, and sulphur monochloride, but not in silicon tetrachloride or stannic chloride. Bismuth was attacked in chloroform, phosphorus trichloride, arsenic trichloride, sulphur monochloride, but not in carbon tetrachloride, ethyl chloride, or stannic chloride. Copper was tarnished in ethyl chloride, but remained unattacked in chloroform, carbon tetrachloride, ethyl chloride, silicon tetrachloride, stannic chloride, and phosphorus trichloride. Silver was plated black in ethyl chloride and antimony pentachloride, but not in chloroform, carbon tetrachloride, or silicon tetrachloride. Antimony was attacked in chloroform, and ethyl chloride, but not in carbon

tetrachloride, stannic chloride, phosphorus trichloride, or arsenic trichloride. Gold, platinum, and palladium were unattacked in chloroform, carbon tetrachloride, ethyl chloride, stannic chloride, phosphorus trichloride, antimony pentachloride, sulphur monochloride, or thionyl chloride. Arsenic was unattacked in chloroform, carbon tetrachloride, ethyl chloride, stannic chloride, arsenic trichloride, antimony pentachloride, or sulphur monochloride. Tellurium was unattacked in chloroform, carbon tetrachloride, ethyl chloride, silicon tetrachloride, stannic chloride, phosphorus trichloride, arsenic trichloride, or antimony pentachloride.

For further details the reader is referred to the original paper, but it may be mentioned here that in the cases of aluminium and magnesium the admission of small traces of water was not sufficient to cause a benzene solution of hydrogen chloride to act on the metals.

Hydrogen Chloride and Ammonia, etc.—It was found by Kahlenberg¹ that when anhydrous benzene was treated with hydrogen chloride which had been first dried over sulphuric acid, and then for some time over phosphorus pentoxide, and then with dry ammonia, a white precipitate of ammonium chloride was at once formed. Moreover, the benzene vapours were quite sufficient to cause a reaction to proceed between the dry gases.

In a similar way, anhydrous pyridine mixed with benzene gave a heavy white precipitate of pyridine hydrochloride when hydrogen chloride gas was passed in.

Hydrogen Chloride and Salts.—According to Hughes,² dried hydrogen chloride produced only a slight turbidity with a solution of silver nitrate in hot dry benzene or ether. With alcohol as solvent, the amount of precipitate was somewhat greater. However, Kahlenberg has pointed out that silver nitrate is almost insoluble in both benzene and in ether, so very little precipitate would be expected in any case.

It was found by Kahlenberg that a solution of dry hydrogen chloride in dry benzene did not attack sodium carbonate, calcite, or witherite. In the cases of calcite and witherite, this has been shown by Patten³ to be also true of dry solutions in chloroform, carbon tetrachloride, ethyl chloride, stannic chloride, silicon tetrachloride, phosphorus trichloride, arsenic trichloride, antimony pentachloride, and sulphur monochloride. With a solution of hydrogen chloride in thionyl chloride, however, they were attacked vigorously, with evolution of gas.

Kahlenberg also found that dry hydrogen chloride instantly

¹ *Loc. cit.*

² *Phil. Mag.* (v.), **35**, 531 (1892).

³ *Loc. cit.*

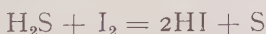
gave a heavy brown precipitate when passed into a dry benzene solution of copper oleate. Similar results were obtained with nickel and cobalt oleates. Stannic chloride, phosphorus trichloride, arsenic trichloride, and silicon tetrachloride had the same effect as hydrogen chloride in these reactions.

It was shown by W. D. Patton¹ that dry hydrogen chloride dissolved in dry benzene would not react with dry soda-lime, and that an infinitesimal amount of water was not sufficient to cause the reaction to proceed.

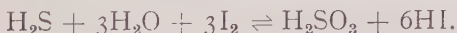
Hydrogen Sulphide and Salts.—Also according to Kahlenberg, dry hydrogen sulphide gave precipitates of heavy metal sulphides when passed into dry benzene solutions of copper, nickel, and cobalt oleates. Stannic chloride dissolved in benzene gave no precipitate immediately with hydrogen sulphide, but on standing overnight a precipitate did form. Arsenic trichloride showed the same reluctance to react.

Hydrogen Sulphide and Iodine.—It was mentioned by Noyes and Sammet² that the decoloration of a dry ethereal solution of iodine is caused only very slowly by hydrogen sulphide, but takes place very quickly when water is added.

The reason for this, however, is now obvious. A more detailed investigation of this reaction was carried out by Parsons,³ who showed that although the reaction was so much slower in the absence of water, it went to completion under these conditions, whereas in the presence of water it was incomplete, the equilibrium point reached depending on the water content of the solvent. In anhydrous ether, the reaction was shown to proceed according to the equation



whereas in the presence of water a series of consecutive reactions occur, which may be formulated



Hence it is obvious that this is not a true effect of the type we are discussing, but it is mentioned here in order to indicate that several, if not all, the other examples dealt with in this chapter may have an equally simple explanation. This the future may decide.

Iodine and Metals.—The reactions between several metals and iodine, with the latter dissolved in various dry solvents, were

¹ *Vide* H. E. Patten, *J. Physical Chem.*, **7**, 158 (1903).

² *J. Amer. Chem. Soc.*, **24**, 498 (1902).

³ *Ibid.*, **47**, 1820 (1925).

investigated by Parsons.¹ A close parallelism was found to exist between the ability of a liquid to bring about the reaction between a metal and iodine, and the solubility of the metallic iodide in the liquid. It was concluded that the only logical explanation of the function of the water and other solvents which produce the reaction is that it removes the film of solid iodide from the surface of the metals and allows more iodine to come into contact with the metallic surface.

¹ *J. Amer. Chem. Soc.*, **47**, 1830, (1925).

CHAPTER XV.

THE DECOMPOSITION OF SOLIDS.

The Thermal Dissociation of Mercurous Chloride.—With the object of investigating whether the phenomena he had observed with ammonium chloride were of a general character, Baker carried out similar experiments with calomel.¹ Pure mercurous chloride was dried at 110° and then kept in a desiccator in a dark cupboard. Vapour density determinations were made by Victor Meyer's method in a hard glass apparatus of the form shown in Fig. 11. A bent tube, in which plugs of phosphorus pentoxide were placed, was ground to fit the neck of the apparatus. A small hard glass tube containing a known weight of mercurous chloride rested on a glass spoon, the shaft of which was ground into a side tube fused to the neck of the apparatus. By turning the shaft of the spoon, which projected from the side tube, the substance could be made to fall into the bulb of the apparatus.

The whole apparatus was heated to dull redness whilst a current of nitrogen dried by sulphuric acid was passed through it, the delivery tube being then sealed. The tube containing mercurous chloride was then introduced, and the phosphorus pentoxide tube, previously filled with dry nitrogen, put into position. No lubricators were used, mercury seals being placed over the two ground joints.

The closed apparatus was left in the dark for three weeks. The tube was then heated in a sulphur bath. The delivery tube was dipped into a trough containing mercury which had just been boiled. The point of the delivery tube was not broken until there was a considerable excess of pressure in the apparatus, so as to diminish the chance of a trace of moisture diffusing from the dried mercury into the bulb.

The results of the five determinations of the vapour density were 217.7, 222.8, 221.3, 223.9, 201.4; Mean 217.4. The value for no dissociation is 235. A similar experiment carried out in

¹ *J. Chem. Soc.*, **77**, 646 (1900).

nitrogen dried only by means of sulphuric acid gave a vapour density of 118.4. Hence the dissociation was much hindered by removing the moisture as far as possible.

Some confirmation of this result was obtained by heating, in the same air bath, the purified calomel in a nitrogen vacuum in two tubes containing gold leaf, one dried by phosphorus pentoxide, the other not specially dried. No amalgamation of the

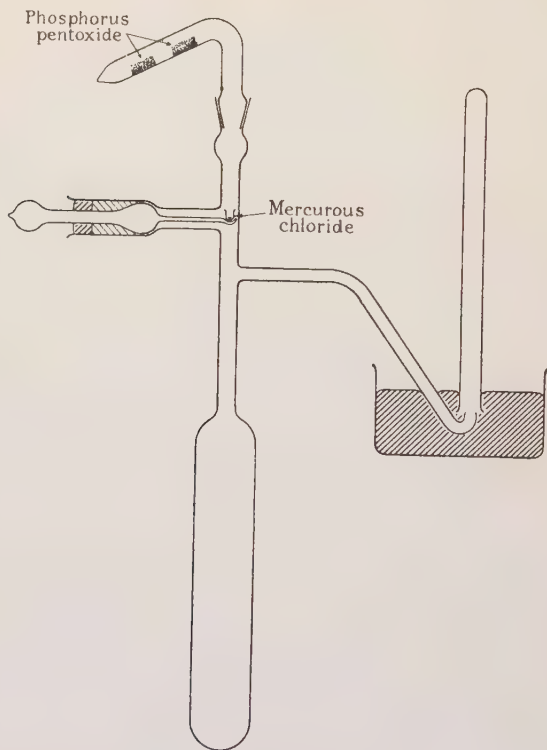


FIG. 11.

gold was seen in the dried tube, whilst in the other the gold had been freely attacked.

The vapour density of dry calomel has also been studied by Smith and Menzies¹ who used a similar method to that used by them for their investigations on ammonium chloride. A weighed amount of calomel was placed in one bulb of a sealed glass apparatus which comprised two further bulbs; one contained

¹ *Z. physikal Chem.*, **76**, 713 (1911).

phosphorus pentoxide and the other, larger, bulb was destined to determine the vapour density of the calomel. The whole apparatus was exhausted and cooled. It was then placed in a thermostat, the temperature of which was kept constant at 115° ; the phosphorus pentoxide bulb, however, was kept at 25° by circulating cold water round it. After $5\frac{1}{2}$ months, the phosphorus pentoxide bulb was sealed off and the apparatus immersed in a constant temperature bath at 352° , and after fifteen minutes the larger bulb was sealed off and weighed. Only one experiment was made, but under such conditions no calomel was found in the large bulb, i.e. the vapour pressure of the extremely dry calomel at 352° appeared to be zero. On the other hand, undried calomel gave normal values corresponding to the composition $\text{Hg} + \text{HgCl}_2$. They considered the result with the dried mercurous chloride to be normal, since they had already shown that in the vapour of mercurous chloride the partial pressure of Hg_2Cl_2 is vanishingly small. They found this result difficult to harmonise with that of Baker. They suggested, however, that one may distinguish between three varieties of mercurous chloride: (a) "not dry" with a normal vapour pressure and vapour density; (b) "dry" (Baker) with double vapour density and the same vapour pressure as the "not dry"; (c) "very dry" (Smith and Menzies) with no vapour pressure.

It has frequently been observed in recent years, however, that changes of state become much slower when the substances are in the intensively dried state. This will be discussed in Chapter XVIII. It appears that this may have been the principal reason why Smith and Menzies found no calomel vapour in the bulb. If they had only waited a longer time before sealing off the bulb, they would probably have found a result more in harmony with that of Baker.

Phosphorus Pentachloride.—Baker found that considerable difficulty was experienced in the investigation of the dissociation of phosphorus pentachloride owing to the fact that it could not readily be obtained in the pure state.¹ Early experiments all pointed to a complete dissociation on heating, but a purer specimen gave at 440° a density of 89.2, that calculated for no dissociation being 104.2. Hence Baker considered that if pure enough, phosphorus pentachloride would be shown to undergo no dissociation on heating.

The Dissociation of Auric Chloride.—When carefully dried, auric chloride, like calomel, exerts a lower dissociation pressure

¹ *J. Chem. Soc.*, **77**, 646 (1900).

than when moist. This was first discovered by Rose¹ during a series of careful experiments on the synthesis and dissociation of the chlorides of gold. The investigation was carried out in a very simple apparatus of the type shown in Fig. 12.

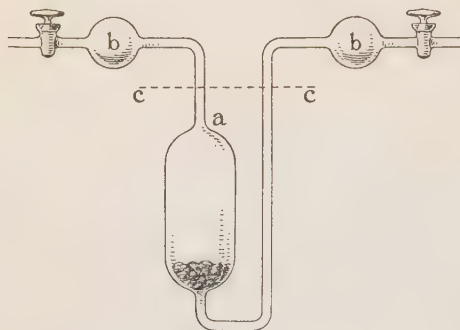


FIG. 12.

Gold leaf was placed in the bulb, and the latter drawn out and sealed as at *a*. The bulbs *b*, *b* contained phosphorus pentoxide, and the tube was heated in an oil bath up to *cc*. Gold chloride was formed inside the tube by passage of a stream of pure chlorine. The dissociation pressure of this chloride was determined

at a few temperatures and found to be normal. The tube was exhausted and heated at 180° to 200° during six weeks, some of the chlorine being pumped out occasionally to aid in removing the moisture. All tubes were heated at intervals by a Bunsen flame. The dissociation pressures subsequently obtained are shown in Table XX.

TABLE XX.

Time of Drying.	Temperature, °C.	Dissociation Pressure.	
		Dried.	Undried.
14 days	194	86 mm.	108 mm.
6 weeks	177.5	42 "	59 "
"	204.0	101 "	150 "

He observed that the pressures given by the dried chloride were only reached after several hours' heating, whereas those of the undried material were attained in less than an hour. Hence drying the gold chloride seemed to retard the attainment of maximum dissociation pressure. The reverse reaction was also tried, chlorine being removed as far as possible with the tube at 270°. The vessel was then cooled and filled at 600 mm. with chlorine which had been dried over phosphorus pentoxide for six weeks.

¹ *J. Chem. Soc.*, **67**, 893 (1895).

The apparatus was then heated; a rise of pressure occurred up to 75° , when it began to diminish. In half an hour, when the temperature had been increased to 220° , the pressure fell to 350 mm. Hence Rose concluded that dry chlorine attacks gold. Unfortunately the experiment was concluded at this stage, whereas perhaps the most interesting aspect of the problem would have been solved if the system had been kept at 220° for some hours, as it would then have been observed whether the pressure fell to the same value as the dissociation pressure of dry auric chloride at that temperature.

The Decomposition of Potassium Chlorate.—Careful experiments were undertaken by Baker¹ in order to ascertain whether the rate of thermal decomposition of potassium chlorate was affected by careful drying, but no difference could be detected between the behaviour of the wet and dry salt. He purified it by several crystallisations, and heated to incipient redness to get rid of the moisture. A small quantity was placed in a hard glass tube already dried, and into which plugs of phosphorus pentoxide had been introduced. The tube was sealed at one end and drawn into a conducting tube at the other. The potassium chlorate was heated in the tube for many hours at about 250° C. to drive off the moisture, the part of the tube containing phosphorus pentoxide being kept cool. After three weeks, the end of the conducting tube was broken under dried mercury, and the potassium chlorate heated. The decomposition took place, apparently, without any difficulty. The gas evolved did not attack mercury, and there was no alteration in volume on addition of a trace of water. It was therefore ordinary oxygen.

Silver and Mercuric Oxides.—Baker also carried out similar experiments on dried silver oxide, but similar results were obtained, no difference being observed in the readiness of the decomposition of the "moist" and "dry" oxides. According to Purcell, Baker has also found that mercuric oxide decomposes at the normal rate even after drying for twenty years.²

The Action of Light on Silver Chloride.—It was found by Baker³ that pure dry silver chloride was not darkened in bright sunlight after it had been sealed up for a few days in a tube containing phosphorus pentoxide in either a vacuum or in an atmosphere of oxygen. In the case of a similar specimen of silver chloride sealed in a tube with pure carbon dioxide which

¹ *J. Chem. Soc.*, **65**, 617 (1894).

² *Ibid.*, 1928, 1213.

³ *Ibid.*, **61**, 728 (1892).

had been dried only by sulphuric acid, a slight change in colour occurred on exposure to light, but this was reversed in darkness.

Simultaneously, Hughes¹ made the same discovery. He found that silver chloride prepared in the dark and dried carefully in an air bath, and then placed on a watch glass in a desiccator partially evacuated, was not perceptibly darkened in sunlight even after an exposure of some hours, whereas rapid darkening took place when moisture was introduced.

¹ *Phil. Mag.* (v.), **35**, 531 (1893).

CHAPTER XVI.

MISCELLANEOUS OTHER EFFECTS.

The Influence of Moisture on Electrical Phenomena.—One of the most interesting aspects of the subject, but one which appears to have been sadly neglected, is the extraordinary effect which traces of moisture seem to be capable of exerting on the phenomena which are observed during electrical discharge. The data upon this subject is extremely scanty, and it would appear to furnish an excellent field for future research.

It was first noted by Warburg¹ that the cathode fall, i.e. the potential difference between the cathode and the dark space, was greater in dry nitrogen than in damp (410 volts instead of 260 volts). On the other hand, in hydrogen the reverse was found to be the case, the cathode fall in the damp gas being greater than in the dry gas (352 volts as against 329).

Sir J. J. Thomson² found that in dry hydrogen the potential difference required to produce a first spark was often more than twice that required to maintain it when once started. Hence the dry gas seemed to be in an unstable condition, which was broken down on the passage of the first spark. This effect was confirmed by Baker.³ Thomson explained this phenomenon by supposing that the passage of a luminous discharge through a dry gas is preceded by the condensation of some of its molecules into a more complex state of aggregation, and that when these aggregates are formed, the potential difference the gas can support has the normal value; also that the formation of these aggregates requires, or is very much facilitated by the presence of nuclei or of a foreign substance, and that when these nuclei are removed or very much diminished in number, the gas can sustain an abnormally large potential difference without its molecules condensing into these aggregates, the gas, however, being in

¹ *Ann. Phys. Chem.*, **31**, 545 (1887).

² *Phil. Mag.* (v.), **36**, 320 (1893).

³ *J. Chem. Soc.*, **65**, 611 (1894).

an unstable condition, for as soon as condensation takes place the potential difference sinks to its normal value.

If sparking were started by means of a brush discharge, much less difference was observed between the wet and dry gases.¹ Several hours were often required before the gas returned to its inactive state.

The removal of water vapour also gradually removes the phosphorescent after-glow in an oxygen tube through which a discharge was passed. On the other hand, it increases this glow in air, which when dried carefully gives a bright glow like that of moist oxygen.

It was found by Baker² that dried ammonia and dried hydrogen chloride can be partially separated from a mixture of the two when oppositely charged plates are placed in the mixture, the ammonia passing to the negative plate and the hydrogen chloride to the positive. Similarly in the case of dried air, oxygen passed towards the positive plate, as it did also with dried electrolytic gas.

Baker also found that the glow produced by shaking mercury with gases disappeared after about two days' drying.

Miscellaneous Effects with Chlorine.—A subject which has been very much to the fore in recent years is the question as to whether dry chlorine behaves in the same way towards actinic light as the moist gas. It was first observed by Budde³ that chlorine undergoes a photo-expansion on illumination. This, he found, could be explained on the basis of a temperature rise; he considered that the light brought about some loosening in the chlorine molecules, and that when the molecules reverted to their normal state this energy was evolved as heat. These observations were confirmed and extended by Richardson.⁴ In 1894, however, Baker seems to have found that there was no photo-expansion with pure chlorine. Discussing the Draper effect, he says, "I have undertaken some experiments with unmixed chlorine, and I have found that in this case there is absolutely no increase in volume."⁵

The Budde effect in dry chlorine was investigated by Shennstone.⁶ He prepared his gas by electrolysis of silver chloride, and dried his apparatus by heating and sweeping out with dry chlo-

¹ *British Assoc. Report*, 1894, p. 482.

² *Loc. cit.*

³ *J. prakt. Chem.* (ii.), **7**, 376 (1873).

⁴ *Phil. Mag.*, **32**, 277 (1891).

⁵ *British Assoc. Report*, 1894, p. 493.

⁶ *J. Chem. Soc.*, **71**, 471 (1897).

rine. A thread of molten silver chloride was used to indicate any volume change. With this arrangement a very small Budde effect was observed, but when a very small amount of moist air was added this was very greatly increased. Hence he concluded that pure dry chlorine did not exhibit the Budde effect. Similar results seem to have been obtained later by Mellor.¹

Experiments on the transparency of chlorine to actinic light appeared to support the view that the behaviour of dry chlorine under illumination was very different from that of moist chlorine under similar conditions. Thus Cordier² found that whilst moist chlorine was comparatively opaque to the actinic light which causes the blackening of silver chloride, dry chlorine was much more transparent to these rays. Mellor³ also found that dry

chlorine was more transparent to actinic light than the moist gas. In view of later work it may be advantageous to describe Mellor's experiments in some detail. The insolation vessel of Bunsen and Roscoe's actinometer *ABC* (Fig. 13) was fitted up in the middle of a large globe, *D*, filled with chlorine gas. The large

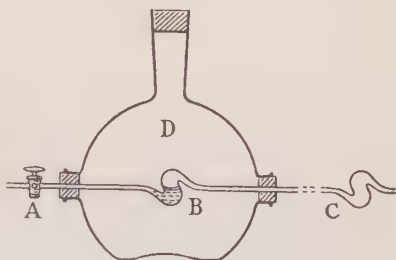


FIG. 13.

globe was painted in such a way that the insolation vessel could be illuminated by a beam of light which had been filtered through a depth of 10 to 15 cm. of chlorine gas. The results

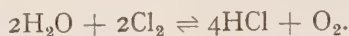
TABLE XXI.

Time, Minutes.	(i.) Air in <i>D</i> .	Index Movement. (ii.) Dry Cl_2 in <i>D</i> .	(iii.) Moist Cl_2 .
8	2	0	No action observed.
9	1	0	
10	3	0	
11	8	0	
12	13	0	
13	12	0	
14	14	0	
15	16	0	
16	18	1	
20	18	2	

obtained are shown in Table XXI. The dry chlorine had been in contact with the purified phosphorus pentoxide for five months.

¹ *J. Chem. Soc.*, **81**, 1280 (1902).² *Monatsh.*, **21**, 660 (1900).³ *Loc. cit.*

The explanation which Mellor offered to account for this apparent greater transparency to actinic light was that some of the energy absorbed by chlorine in the moist state is devoted to maintaining the chemical equilibrium :—



On the other hand, several investigators¹ have failed to detect any difference between the absorption coefficient of moist chlorine and that which has been dried thoroughly. Kistiakowsky found² that extreme drying of the gas did not alter appreciably the structure of its absorption spectrum or the total amount of energy absorbed. He considered that less than 5 per cent. of the absorbed light energy was re-emitted as fluorescence by the dried chlorine. He suggested that the halogens are dissociated into atoms on absorption of light energy in the region of continuous absorption, independently of their degree of purity, and he assumes water to have a catalytic effect on the rate of re-combination of the atoms, and hence on the rate of thermal dissociation of the chlorine molecules.

Weigert and Nicolai³ came to the conclusion that the observations that the light absorption of moist and dry chlorine is identical were only reconcilable with the experiments of Cordier and of Mellor, if there was quite considerable fluorescence in the dry chlorine. Hence Mellor's experiment was repeated, with the difference that the actinometer was not included in the bulb containing the chlorine, but that the latter gas was enclosed in a separate cylindrical tube, which could be moved up and down into different positions between the light source and the actinometer. The end plates of the chlorine filter were of such cross-section that in all positions it allowed the whole of the pencil of rays employed to pass through it. Now, if fluorescence is produced in dry chlorine, causing the chlorine filter to act as a secondary light source, it would be expected that the combination of the hydrogen and chlorine in the actinometer would be greater with the filter near the actinometer than it would be at a further distance from it. Actually Weigert and Nicolai found, however, that the movement observed when the filter was near the actinometer was only 60 per cent. of that observed when it was some distance

¹ Le Blanc, *Zeit. Elektrochem.*, **25**, 234 (1919); Halban and Siedentopf, *Z. physikal. Chem.*, **103**, 71 (1922); Kornfeld and Steiner, *Z. Physik*, **45**, 325 (1927).

² *J. Amer. Chem. Soc.*, **49**, 2194 (1927).

³ *Z. physikal. Chem.*, **131**, 267 (1928).

away. No comparative experiments were carried out, however, between the effects of moist and dry chlorine.

These observations are supported by the experiments of Martin and Cole,¹ who, according to Martin, Cole, and Lent² carried out their investigations on the scattering of light by chlorine with both the commercial and dried material, and found no difference between the intensities obtained. Both scattered quite normally, i.e. the intensity of the scattered light agreed with that calculated from the Rayleigh formula, and was a thousandfold less than any hypothetical isochromatic fluorescence which would be required to explain Shenstone's results.

Martin, Cole, and Lent found that no fluorescence could be observed in chlorine when illuminated by a powerful beam from

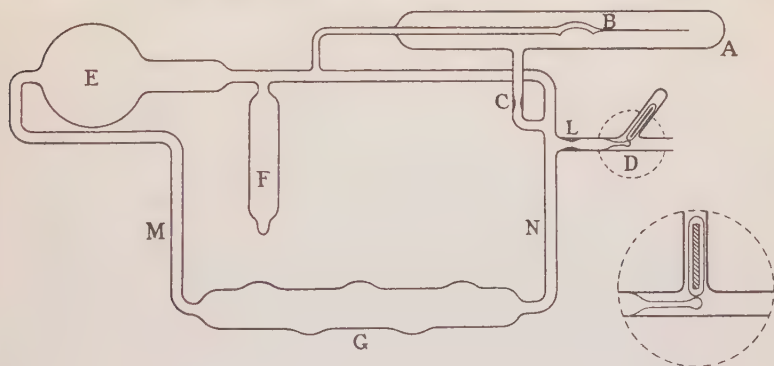


FIG. 14.

a carbon arc. The chlorine was dried intensively by long exposure to phosphorus pentoxide, and the pressure was then lowered by condensing the chlorine into a side arm by means of liquid air. As the pressure decreased, the intensity of the scattering also fell off gradually, and disappeared without showing any increase which might be called fluorescence.

They then proceeded to measure the Budde effect in dry chlorine, since they could not reconcile the fact of the complete disappearance of the Budde effect with the observations that the other properties were not at all changed. The energy must emerge in some form. The apparatus used is shown in Fig. 14. All was made of Pyrex glass, except the glass spring indicator, which was made from soft glass and joined to the Pyrex by a

¹ *Trans. American Electrochem. Soc.*, **49**, 135 (1926).

² *J. Physical Chem.*, **33**, 148 (1929).

graded seal. Phosphorus pentoxide was distilled at about 400°C . over platinised asbestos in a current of oxygen from several sidearms into *G*. The whole was tested for leak-tightness, and evacuated while baked out in a Bunsen flame. The expansion bulb *E* was baked out in an electric muffle at 425°C . for two hours under a high vacuum. The apparatus was then sealed up. Chlorine, purified by fractionation, was admitted at *D* by breaking the seal with a breaker operated electro-magnetically. The sampler tube showed a purity greater than 99.999 per cent. The light from a powerful carbon arc lamp was focussed on the bulb *E* (150 c.c. capacity), and the movements of the gauge were read. After chlorine was first admitted, the gauge showed, on illumination of the gas, an increase of pressure of 10.5 mm. of

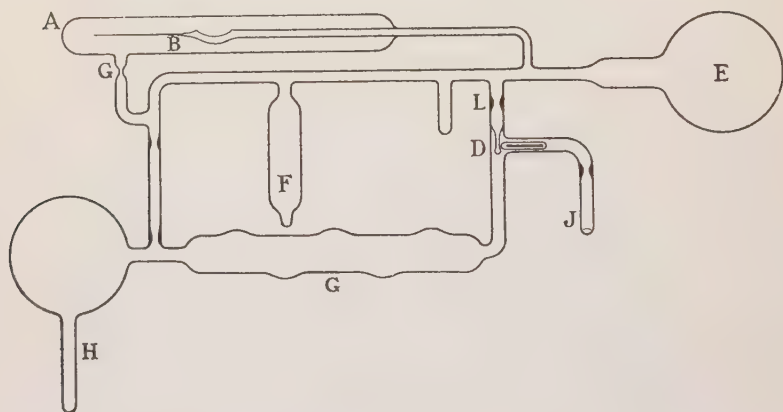


FIG. 15.

mercury. The pointer moved to its maximum reading about thirty seconds after the light was turned on, and returned to its original position in about the same time after the light was extinguished. Air in the apparatus showed no such expansion. Bulb *E* and tube *M* were then warmed to about 34° , and tube *N* cooled to about 8°C . Circulation was such that the whole of the chlorine passed over the phosphorus pentoxide every thirty minutes. Circulation was continued for 250 hours, distributed over thirty days. Readings of the photo-expansion were taken periodically, and gave values such as: 20 hours, 10.5 mm.; 50 hours, 9.5 mm.; 100 hours, 11 mm.; 200 hours, 9 mm. Thus there was no decrease in the expansion effect on drying; the variations observed were doubtless due to variations in the light source. Owing to the possibility that water might cling to

the walls of the vessel *E*, a second apparatus was made (Fig. 15) in which *E* could be baked out thoroughly, and then the chlorine from the circulation apparatus introduced only after long drying. The expansion bulb was baked out at 425° C. under high vacuum for four days. Purified chlorine was admitted to the drying chamber, where it was circulated by alternately condensing it with liquid air into *H* and *J*, which also contained a little phosphorus pentoxide. Drying was continued for twenty-two days, circulation being carried out twenty times. The dried gas was condensed into *H*, seal *D* broken, the gas all condensed into *F*, and the photo-expansion part sealed off at *L*. Since the drying section and the expansion section of the apparatus had been made so as to have equal volumes, the pressure of the chlorine was then atmospheric. On exposure to the light, a pressure increase corresponding to 15 mm. of mercury was observed.

Hence Martin, Cole, and Lent claim that these experiments disprove the conclusion drawn by several of the previous workers, and indicate that the Budde effect in chlorine is independent of the presence of water vapour.

Similar results have also been obtained by Kistiakowsky.¹

The Budde Effect, etc., in Bromine.—It was found by Ludlam² that ordinary bromine showed the Budde effect, but that after quite rough drying with phosphorus pentoxide none was observed, even when very powerful light sources were employed.

This work was developed by Lewis and Rideal,³ whose results indicated that the Budde effect was proportional both to the partial pressure of the bromine and also to that of the water vapour. Table XXII. shows the Budde effect in bars (dynes per sq. cm.) which they obtained at a constant bromine pressure of 158 mm. and a temperature of 40° C., with varying partial pressures of water vapour. The light source was a 1000 c.p. point light, parallel rays being obtained with a collimator. The lamp was 15 cm. distant from the absorption vessel.

The maximum attained was due to the complete absorption of the active radiation by the system. It was concluded that the Budde effect was due to a photoactive bromine hydrate, $\text{Br}_2 \cdot \text{H}_2\text{O}$. The departures from the effects which would be expected therefrom were explained by supposing the hydrate to be strongly adsorbed by glass surfaces. The relationship between the concentration in bulk and in the surface phases,

¹ *J. Amer. Chem. Soc.*, **51**, 1395 (1929).

² *Proc. Roy. Soc., Edinburgh*, **44**, 197 (1924).

³ *J. Chem. Soc.*, **129**, 583, 606 (1926).

they found, could be expressed as an adsorption isotherm. The hydrate, they supposed, could be displaced from glass surfaces

TABLE XXII.

Pressure of Water, in mm. Hg.		Deflection in Bars.
0		0
3.9	$\times 10^{-5}$	66
2.3	$\times 10^{-4}$	226
5.0	$\times 10^{-3}$	958.8
4.15	$\times 10^{-2}$	1640
8.3	$\times 10^{-2}$	1830
1.245	$\times 10^{-1}$	1950
1.66	$\times 10^{-1}$	2020
3.32	$\times 10^{-1}$	2140
5.395	$\times 10^{-1}$	2140

by water. The Budde effect was not observed at all on illuminating moist bromine with light of wave-length longer than 5800μ .

Assuming bromine hydrate to be the cause of the Budde effect, Lewis and Rideal calculated the heat of formation of this hydrate from the extent of the Budde effect at various temperatures. The value deduced in this manner was 1090 calories, a figure comparable with the heat of solution of bromine in water. The equilibrium constant for the dissociation of the hydrate at 313° abs. was calculated to be of the order of 3.10×10^9 . Marked absorption of light was found to commence at $\lambda = 6100 \text{ \AA.}$ for wet, and at 5700 \AA. for dry bromine, corresponding to a lowering of the critical energy increment of excitation of 3200 calories.

Some doubt has been cast on whether moisture really exerts any influence on the promotion of the Budde effect in bromine owing to some recent investigations by Brown and Chapman.¹

TABLE XXIII.

Light filtered through 25 per cent. ferrous ammonium sulphate solution:—

Time of drying (days)	Wet	79	396
Expansion (scale divisions)	57	50.6	53.5

Ratios of Expansion caused by exposure to light which has been filtered through a 5 per cent. solution of sodium dichromate to that occasioned by exposure to light transmitted by 25 per cent. ferrous ammonium sulphate:—

Time of Drying (days)	.	Wet	22	61	72	126	396
Ratio of Expansions	.	0.40	0.39	0.44	0.41	0.38	0.35

From a very careful series of experiments, results were obtained which indicate that the Budde effect with a mixture of air and bromine is not diminished to any measurable extent by drying.

¹ *J. Chem. Soc.*, 1928, 560.

The movement of a short thread of bromine was observed in a capillary tube between two bulbs, one being insulated and the other darkened. Comparison was made with a "wet" mixture. Typical results obtained were as shown in Table XXIII.

On the other hand, some confirmation of the results of Lewis and Rideal has been obtained by Matthews¹ who showed that dry bromine could show very considerably less Budde effect than the dry gas, the effect of drying being much more pronounced with the pure vapour alone than when the bromine vapour was mixed with air. During the period of drying employed (eight weeks) the effect did not disappear completely, but it was reduced to about a quarter of that with the dry gas.

Kistiakowsky, however, agrees with Brown and Chapman, finding no change whatever in the effect on adding water vapour after drying either by low temperature distillation or by means of phosphorus pentoxide.²

The Combination of Hydrogen Atoms.—It has been shown spectrographically by R. W. Wood³ that hydrogen atoms cannot survive in a glass tube through which an electric discharge is passed if the walls are quite dry. This fact he explained by supposing that the hydrogen atoms recombine on the surface of the dry glass, whereas the presence of moisture protects them from this action.

The Reduction of Organic Compounds by Nascent Hydrogen.—It was observed by Otto⁴ that a number of organic substances such as benzosulphonic chloride, phenylic disulphoxide, phenylic bisulphide, *p*-toluene sulphonic chloride, and benzene sulphonic acid, whilst readily reduced by nascent hydrogen in the presence of water, were not reduced when water was excluded.

¹ *Trans. Faraday Soc.*, **25**, 41 (1929).

² *J. Amer. Chem. Soc.*, **51**, 1395 (1929).

³ *Proc. Roy. Soc.*, **102A**, 1 (1922).

⁴ *Ber.*, **26**, 2050 (1894).

CHAPTER XVII.

SUMMARY OF THE THEORIES OF THE ACTION OF WATER VAPOUR IN PROMOTING CHEMICAL REACTION.

IN concluding the first section of this volume, it appears advantageous to give a short summary of the various theories which have been put forward to account for the influence of water vapour on the progress of chemical reactions. Many of these theories have been dealt with to some extent already, when their application to certain reactions has been discussed. The theories dealt with below, however, include only those of general applicability, or of a characteristic type. It is much to be regretted that the majority of the theories which have been put forward at various times have been of a rather specific nature, to explain the action of the water vapour in a particular system, and few chemists have attempted to formulate theories to apply to the phenomenon in general. It seems very obvious that any theory to be of much utility in this connection must be of a more or less general character.

Intermediate Compound Theory.—The first attempt made to account for the influence of moisture in promoting chemical reaction seems to be that of William Higgins,¹ who found that iron did not rust in dry oxygen, and suggested that “. . . it is the oxygen of the water which unites to it, while the oxygen of the gas is condensed by the liberated hydrogen in its nascent state, so as to reproduce water. This is effected by a double influence which is so obvious as not to require an explanation. . . . The process of bleaching is effected in this way.”

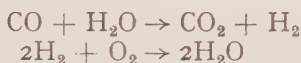
A very similar explanation was also given quite independently by Mrs. Fulhame² to account for the action of moisture in causing hydrogen to reduce the oxides of gold, etc. She supposed that the hydrogen of the gas united with the oxygen of the water,

¹ *Comparative View of the Phlogiston Theory*, 1791; *Experiments and Observations on the Atomic Theory*, 1814.

² *Essay on Combustion*, 1794.

whilst the hydrogen of the latter united in its nascent state with the oxygen of the metal, reducing it and forming water. She also quoted the early observations of Bergmann and Scheele, considering that they proved her theory that water was essential both for the reduction and oxygenation of bodies, and that it was always decomposed in these reactions. She supposed that these two reactions always occurred simultaneously, and that in combustion one body is oxidised by the oxygen of the water, whilst another is restored to its combustible state by the hydrogen of the same fluid.

Much the same mechanism was suggested independently almost a century later by Dixon¹ to account for the influence of moisture on the reaction between carbon monoxide and oxygen. He supposed that this reaction took place in two stages as follows :—



The arguments which have been brought forward for and against this theory as applied to this particular reaction have already been discussed. Other intermediate products as well as hydrogen have also been suggested for this reaction, e.g. hydrogen peroxide² and formic acid.³

Similarly, several intermediate compounds have been suggested at various times for the reaction between hydrogen and chlorine, e.g. chlorine monoxide,⁴ hypochlorous acid,⁵ and complexes of water molecules with hydrogen and/or chlorine molecules.⁶ Others have involved water in the chain mechanism for this and other reactions.⁷

The great objection to this theory is that if the water actually takes part in the reaction, either in forming an intermediate compound or in entering into some kind of chain mechanism, the concentration of the water vapour should certainly be of some

¹ *British Assoc. Report*, 1880, p. 503.

² Traube, *Ber.*, **18**, 1890 (1885).

³ Wieland, *ibid.*, **45**, 679 (1912).

⁴ Pringsheim, *Ann. Phys. Chem.* (iii.), **32**, 421 (1887).

⁵ Veley, *Phil. Mag.* (v.), **37**, 170 (1894); Gautier and Hélier, *Compt. rend.*, **124**, 1267 (1897).

⁶ Mellor, *J. Chem. Soc.*, **81**, 1292 (1902); Bevan, *Phil. Trans.*, **202A**, 71 (1903); Weigert, *Z. physikal. Chem.*, **106**, 407 (1923); Marshall, *J. Physical Chem.*, **29**, 842 (1925); Chapman, *Trans. Faraday Soc.*, **21**, 547 (1926).

⁷ Stern and Volmer, *Z. wiss. Photochem.*, **19**, 275 (1920); Coehn and Jung, *Z. physikal. Chem.*, **110**, 705 (1924).

account. However, it has been found by Coehn and Jung that when the water vapour pressure exceeds the very small value of 10^{-3} mm., its concentration has no effect whatever on the rate of the reaction between hydrogen and chlorine.

Solution Theories.—It was suggested by Parnell¹ that the function of water in permitting action between hydrogen sulphide gas and metallic salts was to combine with the acid, which is set free by the sulphuretted hydrogen, immediately on its liberation. He compared this phenomenon with the non-solubility of zinc or iron in concentrated sulphuric acid, supposing that in the latter case water was necessary to combine with the sulphate of zinc about to be formed.

Kolb² attributed to water either a mechanical action or a solvent action in its causing carbon dioxide to react with oxides and hydroxides. He leant towards the latter view, since he showed that carbonisation was slower the less the solubility of the hydroxide in water.

The explanation put forward by Hughes³ to account for the non-reactivity of hydrogen chloride and hydrogen sulphide gases when in a dry state was that these compounds should properly be considered as acid anhydrides and not as acids.

The fact that those reactions which are arrested by quite rough desiccation are mainly of an ionic type, will be discussed later. A theory of this type almost certainly accounts for the influence of moisture on this type of reaction.

Armstrong's "Reversed Electrolysis" Theory.—It was first suggested by A. Vernon Harcourt, during a discussion at the Ashmolean Society at Oxford in 1884, that the explanation of the extraordinary effect of water vapour on chemical reaction should be sought rather from a physical than from a chemical point of view. This appears to have led Armstrong to suggest his explanation, which was first put forward in the same year.⁴ He likened chemical reaction to a reversed process of electrolysis. Thus he likened the action of water in the explosion of carbon monoxide and oxygen to the action of sulphuric acid in Groves' gas batteries. He supposed that in order to cause the reaction between carbon monoxide and oxygen to proceed, it was necessary that the third substance should be divisible between the carbon monoxide and oxygen, and that this division must be

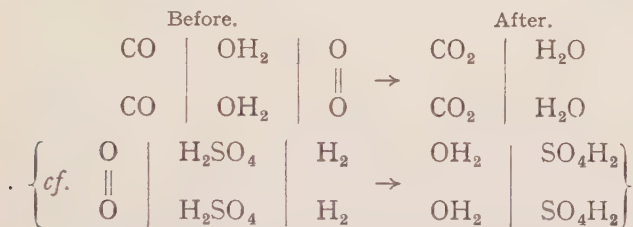
¹ *British Assoc. Report*, 1841, p. 51.

² *Compt. rend.*, **64**, 861 (1867).

³ *Phil. Mag.* (v.), **33**, 471 (1893).

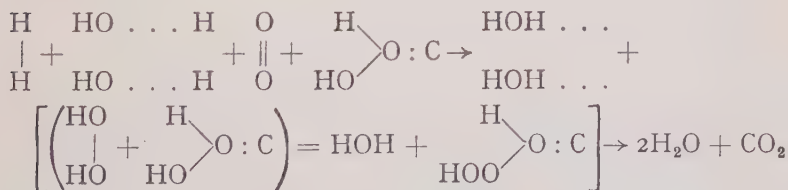
⁴ *Proc. Roy. Soc.*, **40**, 288 (1884); *British Assoc. Presidential Address*, 1885; *J. Chem. Soc.*, **49**, 112 (1886).

into positive and negative radicles. Hence he was led to the suggestion that water might also catalyse the reaction between hydrogen and oxygen. This was confirmed by Baker nearly twenty years later. Armstrong supposed water to form a "closed conducting circuit" owing to the presence of a trace of electrolyte impurity. The oxygen was supposed to act just like a depolarising agent, thus :—



This view supposes that carbon monoxide and oxygen molecules are absolutely inert towards one another. He predicted that similar observations of the necessity of moisture for the progress of the reactions would be observed in the cases of the combination of hydrogen and chlorine, of nitric oxide and oxygen, and as has already been mentioned, of hydrogen and oxygen. This, however, appears to be the only direction in which Armstrong's Theory has received any support, for although these predictions have all been proved experimentally, there is no other evidence to lend support to this theory.

Even as recently as 1925,¹ Armstrong has declared carbon monoxide to be "*per se* an incombustible gas," and he still appears to hold to his former view that the same is true of the other gaseous reactions mentioned. He now writes the equation representing the reaction in a somewhat more complicated form, however, thus :—



This theory, especially in this form, could well have been classified among the intermediate compound theories, but it seems to be of a sufficiently distinct type to warrant a separate mention.

¹ *Proc. Roy. Soc.*, **98B**, 202 (1925).

Electrical Force Theories.—It was first suggested by Sir J. J. Thomson¹ that the influence of water vapour on chemical reactions was of an electrical nature. Supposing the forces holding the atoms in the molecule together to be electrical in character, he pointed out that these forces will be very much diminished when the molecule is close to the surface of, or surrounded by, a conductor or a substance like water possessing a very large specific inductive capacity. Let AB , Fig. 16, represent two atoms in a molecule placed near a conducting sphere; then the effect of the electrical charge induced on the sphere by A will

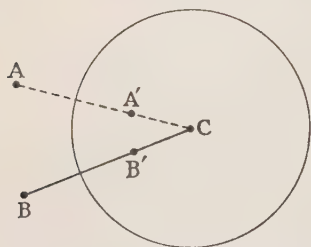


FIG. 16.

be represented by an opposite charge placed at A' , the image of A in the sphere. If A is very near the surface of the sphere, then the negative charge at A' will be very nearly equal to that at A . Hence the effect of the sphere will be practically to neutralise the electrical effects of A ; i.e. the affinity between atoms A and B will be almost annulled by the presence of the sphere. Similar

effects, it was suggested, may possibly explain the fact that in aqueous solution the forces between the atoms in the molecule are much less than when free and in the gaseous state. This theory was developed as a result of the experiments which Thomson had carried out showing the great influence which water vapour exerts on the readiness of the passage of electrical discharges through gases. It appears to agree better than most other theories which have been put forward with the general experimental data, and it is the theory at present favoured by Baker.²

It has also been suggested by Cathala³ that the function of the water molecule, as an electrical dipole with a large stray force field, is to induce greater chemical reactivity in those molecules within its sphere of influence.

A very similar theory, but associating the effect with the surface of the reaction vessel only, has been put forward by Norrish.⁴ He supposes that since the main characteristic of a polar molecule, such as water, is its strong unbalanced field of force, it is probable

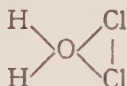
¹ *Phil. Mag.* (v.), **36**, 320 (1893); *British Assoc. Report*, 1894, p. 482.

² *J. Chem. Soc.*, 1928, 1051.

³ *Compt. rend.*, **181**, 33 (1925).

⁴ *J. Chem. Soc.*, **123**, 3006 (1923); **127**, 2316 (1925); *Trans. Faraday Soc.*, **21**, 575 (1926).

that its function as a catalyst is to weaken by close association the intra-molecular forces of the resting molecule and so render it more easily disintegrable. Hence he concludes that those molecules which have formed a close association with the molecules of a catalyst are at least partly activated, inasmuch as they alone are capable of any further chemical reaction. Thus only in the case of these molecules can the supplementary activation necessary for the reaction be attained by collision. Thus in the case of hydrogen and chlorine he supposes that a water-chlorine complex, e.g.



is formed on the surface of the vessel, but is so structurally weakened by adsorption that light can bring about its decomposition into water molecules and chlorine atoms. Whilst weighty arguments can be brought against this theory as applied to the reaction between hydrogen and chlorine, as has already been indicated in Chapter IV., there are still many phenomena for which this theory affords the most satisfactory explanation of any which have yet been put forward. Thus it appears certain that the velocity of combination of the halogens with ethylene is dependent on the polarity of the surface. From the observations of Hinshelwood and Burk, which have already been discussed, it appears that the surface is also of importance in the reaction between hydrogen chloride and ammonia. From the evidence of this experiment, Hinshelwood suggests that this explains why a trace and no more of moisture is needed for gaseous reactions to proceed. He considers that the majority of reactions in which the influence of moisture is marked are reactions in which a boundary surface plays a part.¹

The suggestions made by Taylor² may also be brought under this same category. He supposed that the insensitivity of dried gases to reaction demonstrated that it was not the energy of collision which brings about interaction, since small quantities of water vapour could not alter this magnitude; but that the water vapour molecules, highly polar, must behave in the same manner as do contact catalysts in activating the several molecular species.

Smits' Theory.—It is assumed by Smits³ that every phase of

¹ *School Science Review*, No. 31, 169 (1927).

² *J. Physical Chem.*, **28**, 897 (1924).

³ *Proc. K. Akad. Wetens.*, Amsterdam, **26**, 266 (1923).

substances contains at least two different kinds of molecules, and that these different kinds are in inner equilibrium in the case of unary behaviour. It is further supposed that at least one of these kinds of molecules is chemically active. This he considers to be very well possible, because the mechanism of the transformation into another type of molecule will be entirely different from that of chemical action with other substances. To represent the case as simply as possible he takes the example of two different kinds of molecules, one active and the other inactive. In such a case we have in each phase in the case of unary behaviour an inner equilibrium of the type



He suggests that on intensive drying this inner equilibrium is shifted towards the inactive side, and in this particular case *completely*, so that the ammonia that remains contains only the inactive kind of molecules and so does not combine, say, with hydrogen chloride. In the same way, Smits explains the non-dissociation of ammonium chloride by assuming it to exist in two different forms, one of which dissociates, the inner equilibria being shifted over to this form on intensive drying. He points out that the expression "different types of molecules" must be taken in its widest sense, to include not only isomeric and polymeric molecules, but also the electrically charged dissociation products, ions + electrons, and different atomic structures.

This theory possesses the great advantage over the majority of the other suggestions that have been put forward of being of a much wider application. The cases to which it is particularly applicable are those for which no other satisfactory theory has been advanced, namely, reactions of the type of those between hydrogen and chlorine and between hydrogen and oxygen. Almost certainly it is *not* the explanation of the influence of moisture on the reaction between carbon monoxide and oxygen, nor is it readily applicable to cases such as the reactions between solid and gaseous phases. For such systems, which require a much larger amount of moisture present in order that they may behave normally, we must seek different explanations, but for reactions of the type cited above no other theory explains the facts so simply or so readily. This theory also blends with Smits' Theory of the influence of intensive drying on physical properties, and the experimental support which has been obtained for the latter theory tends to add more weight to the value of the theory as applied to chemical reactions.

Discussion.—The great difference in the degree of desiccation which is necessary to prevent the various reactions from proceeding leads one to suggest that reactions should be divided into several categories. These are of necessity ill-defined, but broad differences can readily be observed. Thus, one characteristic class of reaction which is, generally speaking, influenced by drying, includes the reactions of a more or less ionic character, e.g. the absorption of carbon dioxide by alkaline hydroxides, etc., and the action of gaseous hydrogen chloride on calcspar. The effect of desiccation on these systems can well be understood, inasmuch as they require the presence of a dissociating medium before the ionic reactions can occur. Hence, even rough drying will prevent the reaction progressing to any measurable extent. This explanation is practically the modern interpretation of the theories put forward by Parnell and by Kolb.

On the other extreme we have such reactions as those between hydrogen and chlorine and between hydrogen and oxygen. In these cases a much higher degree of desiccation is required to influence the progress of the reactions than that which generally suffices in the case of the reactions of an ionic type ; it is, in fact, probably of about the same order as that required to produce the abnormalities in physical properties which are discussed in the later chapters of this volume. All gaseous reactions, however, do not belong to this class, since the reaction between carbon monoxide and oxygen, at any rate, has been shown by the work of Bone and Weston to belong to a different type.

Beyond this broad separation it seems impossible to pass at present. Thus it is not at all clear into what classification oxidation and reduction reactions should fall. Doubtless further investigations will throw light on this question, and some simple explanation will be found to account for all these phenomena.

CHAPTER XVIII.

THE INFLUENCE OF INTENSIVE DRYING ON PHYSICAL PROPERTIES.

Baker's Researches.—The first recorded observation of any change in the physical properties of a substance on intensive drying appears to have been that of H. B. Baker and Mrs. Baker,¹ who found that the vapour density of nitrogen trioxide was greater after it had been dried over phosphorus pentoxide for some time. They concluded that the gas obtained contained a higher polymeride, probably N_4O_6 . The vapour density of the dried gas corresponded with a mixture of three molecules of N_4O_6 to one of N_2O_3 .

In 1912 the same authors² announced that nitrogen trioxide which had been sealed up with phosphorus pentoxide for three years, boiled at 42.5° , as against a normal boiling-point of -2° C. Similarly, nitrogen tetroxide, dried for over a year, boiled above 69° , whereas the normal boiling-point is 21.5° C. This was again attributed to a difference in complexity in the "dry" and "moist" liquids.

In order to follow up these observations, Baker, in 1913, sealed up a number of pure liquids in vessels containing purified phosphorus pentoxide. These were left standing for eight or nine years, and were only re-opened in 1921 and 1922. In every case the boiling-point, indicated by the formation of bubbles in the heated liquid, showed a large elevation of 30° to 60° .³

The apparatus used consisted of a distilling flask of Jena glass with two side tubes. To one of these tubes was sealed the side-piece of another distilling flask, whilst the other was drawn out to a long tube about 2 mm. in diameter. The necks of the distilling flasks were lengthened by sealing on tubes of similar diameter, which were bent down at the top to form convenient receptacles for the phosphorus pentoxide. The apparatus was cleaned with chromic and nitric acids, washed with distilled

¹ *J. Chem. Soc.*, **91**, 1862 (1907). ² *Ibid.*, **101**, 2339 (1912).

³ *Ibid.*, **121**, 568 (1922).

water and dried by heating nearly to redness, whilst a current of air, dried by sulphuric acid and phosphorus pentoxide, was drawn through every part. Fragments of fused quartz, previously ignited, were placed at the bottom of each flask, so as to prevent ordinary superheating. After the introduction of the liquids, the openings were sealed, and left for the period of drying. In the cases where no chemical action was feared, e.g. with benzene, hexane, or bromine, one plug of drying agent was placed with the liquid in one of the distilling flasks. In other cases, as with the alcohols and ethyl ether, the drying was dependent on the removal of water from the ever-changing vapour. In no case, even with the alcohols, was any pressure increase noticed when the narrow tube was opened. To determine the boiling-point, the tip of the long tube was dipped under previously boiled mercury, and the depth of the open tube noted. The liquid was distilled by heating the flask containing it in an oil bath, the other flask being cooled in water or ice. When sufficient liquid had been collected in the previously empty flask, the latter was heated in an oil bath, while the other was cooled. The heating of the oil bath was conducted very slowly, so as to allow of the liquid fully attaining the temperature of the oil. When the temperature was approaching the boiling-point, half an hour was occupied in raising the temperature through 5° . The boiling, when it did take place, proceeded quite quietly; no sign of the violent ebullition which accompanies the breaking down of a superheated condition was observed. There was nothing in the behaviour of the liquids, except the reading on the thermometers, which suggested anything abnormal in their boiling. In some cases, two thermometers were enclosed in the bulbs, one dipping in the liquid, and the other suspended about 3 cm. above its surface. The temperatures read on the latter were at most 2° above the normal boiling-point of the liquids, and yet when the condensed liquid from the distillation was again heated, it did not enter into a state of ebullition until the abnormally high temperature had been reached.

Experiments were tried with ten liquids of different types, the results being shown in Table XXIV.

In a later communication¹ Baker announced that further investigation had shown that the difference between the temperatures indicated by his upper and lower thermometers was due to the determination being stopped as soon as an apparently steady condition had been attained. As the contents of a flask of dry

¹ *J. Chem. Soc.*, **123**, 1223 (1923).

benzene were slowly distilled off, the temperature indicated by the thermometer in the vapour rose from 81° to 87° . This seemed to indicate a true fractional distillation, the non-associated liquid coming off first.

In every case the liquid distilled from the dried apparatus was tested for the presence of phosphoric acid, but no trace could be detected. This is of very great importance, as this point has been doubted by Balarev,¹ who repeated Baker's work with methyl alcohol, ethyl alcohol, propyl alcohol, benzene, hexane, and ethyl ether. The liquids were sealed into *U*-tubes, a liquid in one and sublimed phosphorus pentoxide in the other. Subsequent examination of all the liquids showed the presence of

TABLE XXIV.

Liquid.	Period of Drying (Years).	Boiling-point.		
		Original, $^{\circ}\text{C}$.	New, $^{\circ}\text{C}$.	Rise, $^{\circ}\text{C}$.
Bromine	8	63	118	55
Mercury	9	358	420-425	62
Hexane	$8\frac{1}{2}$	68.4	82	14
Benzene	$8\frac{1}{2}$	80	106	26
Carbon disulphide . .	1 + 27	49.5	80	30
Carbon tetrachloride .	9	78	112	34
Ethyl ether	9	35	83	48
Methyl alcohol . . .	9	66	120	54
Ethyl alcohol	9	78.5	138	60
Propyl alcohol . . .	9	95	134	39

phosphoric acid, and he suggested that Baker's rises in boiling-point were due to the presence of this substance or of its esters. Baker has replied to this criticism by repeating that no phosphoric acid could be detected in his dried distillates.² He suggested that Balarev's phosphorus pentoxide may not have been free from the volatile lower oxides. As will be mentioned later, Smits has also shown that the effect is not due to the interaction of the phosphorus pentoxide with the liquids.

Baker also made some vapour pressure measurements, using a dried barometer tube of mercury, surrounded by a water jacket. Dried ether gave at 20° a vapour pressure of 374 mm. instead of 442 mm.

The evidence of the boiling-point and vapour pressure meas-

¹ *J. prak. Chem.*, **116**, 57 (1927).

² *J. Chem. Soc.*, 1927, 2902; *J. prak. Chem.*, **118**, 96 (1928).

urements was considered to suggest that in the liquids there is normally a balance between associated and dissociated molecules, and that the absence of water vapour tends to prevent dissociation. The boiling-point of the dried liquid, consisting mainly of associated molecules, is, as would be expected, much higher than that of the normal liquid.

It was thought that evidence for or against this view would be obtained by measurement of the surface tension of the liquids. This was carried out by the Ramsay and Shield method.¹ The capillaries were attached to their sinkers, washed with nitric and chromic acids and with distilled water, and heated nearly to softening point whilst a current of air was drawn through them; they were then allowed to cool in a desiccator over phosphorus pentoxide. One tube of each pair contained phosphorus pentoxide and the other none. The capillaries used in each case were so selected that they were of nearly the same diameter in each of the pair. In some cases pairs were found of almost identical diameter. The progress of the drying was rendered visible by the greater rise in the capillary tube in the liquid containing phosphorus pentoxide. The actual measurements summarised in Table XXV. were made a year after the tubes had been sealed. It will be noticed that the molecular weight factor in the case of "moist" hexane is given as 0.92. Baker points out that Ramsay and Shields gave 0.93 for *n*-octane, and as there is no possibility of dissociation for these liquids, their so-called "normal" liquids were to some extent associated, and the true value of the constant *k* should be at least 2.28 instead of 2.121.

TABLE XXV.

Liquid.	Multiple of Molecular Weight.	
	"Wet."	"Dry."
Bromine . . .	1.34	1.99
Benzene . . .	1.28	3.39
Hexane . . .	0.92	3.16
Nitrogen tetroxide .	3.00	3.10

Since such remarkable changes were observed in other physical properties, it was thought possible that some change in density might be observed when a liquid was intensively dried. Hence Baker sealed specimens of benzene, carbon tetrachloride, carbon disulphide, ethyl ether, bromine, sulphur dioxide, and nitrogen trioxide into dilatometers containing phosphorus pentoxide, but a year later no volume change of one part in 10,000 could be detected.

¹ *J. Chem. Soc.*, **63**, 1089 (1893).

It may be recalled here that similar observations had been made in the cases of gases. In 1902 Baker mentioned¹ that specimens of hydrogen, oxygen, nitrogen, air, and a mixture of hydrogen and oxygen were dried over mercury by phosphorus pentoxide for six months, but no change in volume was observed. Later² he appears to have extended these experiments in order to test whether polymerisation took place on drying nitric oxide and carbon monoxide similar to that observed in the case of nitrogen trioxide. These gases were introduced into tubes containing phosphorus pentoxide, which were connected with manometers. The tubes were then cooled with liquid air so that the liquefied gases came into contact with the drying agent. The drying at the low temperature was continued for four days. On regaining ordinary temperature again, however, the gases showed no change in volume, so it was concluded that in these circumstances no polymerisation of either of these two gases takes place.

The melting-points of several solids were found to have changed after intensive drying, but the effects observed were by no means so marked as in the cases of boiling-point and surface tension. A summary of Baker's results in this connection is given in Table XXVI.

TABLE XXVI.

Substance.	Period of Drying.	Melting-Points (°C.).		
		Original.	New.	Rise.
Sulphur . . .	10 years	112.5	116.8 to 118.5	4.3 to 6.0
Iodine . . .	9 "	114	116	2
Bromine . . .	10 "	—7.3	—4.5	2.8
Sulphur trioxide				
α -form . . .	18 "	50	61.5	11.5
β -form . . .	18 "	14	15.5	1.5
Benzene . . .	10 "	5.4	6.0	0.6

When first measured, the melting-point of the sulphur was given as 117.5, but on re-investigation in 1923, it was found to give a melting range from 116.8° to 118.5°.

Some vapour density determinations were carried out on the same samples of liquid as were used for the boiling-point measurements. These measurements were made in a modified form of Victor Meyer apparatus, such as was used for the vapour density of calomel (Fig. 11). Ether, dried from 1913 to 1923 (boiling-

¹ *J. Chem. Soc.*, **81**, 400 (1902).

² *Ibid.*, **91**, 1862 (1907).

point $83^{\circ}\text{C}.$ gave a vapour density of 81.7 as against a normal value of 37, and methyl alcohol, dried for the same period (boiling point $122^{\circ}\text{C}.$) gave a vapour density of 45 as against the normal value of 16.

These vapour density experiments have now been considerably extended¹. The liquid was sealed, together with phosphorus pentoxide, into a tube which was connected to a capillary tube in which a series of ten or twelve bulbs of about 15 c.c. capacity were blown. The liquid was then frozen in liquid air, and the whole evacuated. From time to time, as drying progressed, a little liquid was distilled into the end bulb, which was then sealed off and used for vapour density determinations by the same method as before. The following results were obtained:—

TABLE XXVII.

Substance.	Time of Drying (years).	Temperature of Determination, $^{\circ}\text{C}.$	Molecular Weight.	Normal Molecular Weight.
Bromine	2	86	234.3	160
Carbon disulphide	3	93	242.4	160
Carbon disulphide	2	90	127.0	76
Carbon disulphide	4	90	137.4	76
Carbon tetrachloride	3	100	191	154
Carbon tetrachloride	5	100	261	154
Ethyl ether	5	102	173.1	74
Methyl alcohol	5	103	90.6	32
n-Hexane	4	100	160.5	86
Benzene	3	100	102.4	78
Benzene	5	100	125.9	78
Nitrogen tetroxide	10 + 1	80	101.9	92
Nitrogen tetroxide	16 + 5	40	130.7	92

Baker considers that the molecular aggregation in the main mass is probably greater than is represented by the vapour densities in this table, since fractional distillation takes place during the removal of specimens in the small bulbs.

Further evidence still of the increase in the complexity of benzene on intensive drying has been obtained by measurement of its latent heat of evaporation. The method used in its determination will be described in Chapter XX. With two different samples of benzene the latent heats for 1 gram were found to be 37.2 and 58 after the liquid had been dried intensively for three and a half years, instead of the normal 83. The boiling point of the dry benzene was 94° , so to bring this into conformity with

¹ Baker, *J. Chem. Soc.*, 1928, 1051.

Trouton's Rule the molecular weight of benzene must be 136 instead of 78.

Mali has assumed that the dried liquids on which Baker's boiling-point determinations were carried out consisted of a solution of the less volatile form in the normal form.¹ On this supposition, by means of the well-known equation for the elevation of the boiling-point,

$$\frac{x/M}{1 - bx/M} = \frac{L_p \Delta T}{R \bar{T}_0^2},$$

he has attempted to calculate the degree of molecular association in some of Baker's dried liquids. This yielded the results given in Table XXVIII., but the value of these calculations seem rather

TABLE XXVIII.

Liquid.	Density in grams/c.c.	B.P. °C.	L.H. of Evaporation of 1 gram.	T.	$T \frac{x/M}{1 - bx/M}$	Gram Mol. of Moist Liquid in 1 c.c., Molecules supposed to be Normal.
Benzene .	0.879/20° C.	80.2	95.49	26	0.009	0.011
Carbon disulphide .	1.292/0° C.	46.2	85	30	0.016	0.017
Carbon tetrachloride .	1.582/21° C.	76.7	46	34	0.010	0.010
Ethyl alcohol	0.7937/15° C.	78.3	207	60	0.04	0.017
Methyl alcohol	0.796/15° C.	64.7	267	54	0.050	0.025
Bromine .	3.102/25° C.	63	46	55	0.0348	0.0388
Mercury .	13.6/15° C.	356.7	68	62	0.072	0.067
Ethyl ether .	0.718/17° C.	34.6	84	48	0.0152	0.097
Propyl alcohol	0.804/20° C.	97.2	163	39	0.019	0.0133

doubtful. The figures in the last column are calculated on the assumption that the molecules are normally not associated. If association be supposed to exist, these values will be lowered. The true concentration of the solution will be lower than that given in column 6 in the ratio $(1 - bx/M) : 1$. In the cases of benzene, carbon disulphide, carbon tetrachloride, and bromine, the amount of the less volatile component in the dried liquid is very large compared with the amount of the more volatile component. In the cases of the three alcohols, and of ethyl ether, the total number of molecules of the solute in 1 c.c. of the solution (dried liquid) is much greater than the total number of molecules of solvent in 1 c.c. of the moist liquid, unless the value of "b" is very large. If the values of b are of the same order in all the

¹ *Phil. Mag.* (vii.), 5, 609 (1928).

solutions, Mali considers that it must be assumed that in the dried liquid the molecules are dissociated.

Smits' Theory.—In the meantime, whilst these experiments were being carried out, Smits began to see in Baker's results some confirmation of his theory of allotropy. In 1922, referring to Baker's work on nitrogen trioxide and tetroxide,¹ he pointed out ² that the results of these investigations indicated that internal changes in a unary system are strongly checked by intensive drying, or probably are completely stopped, so that a unary system becomes a pseudo-system, of which the ingredients may possibly be separated, e.g. by fractional distillation. He supposed that the mixture would, on distillation, give a distillate with a lower boiling-point than the original liquid. He concluded that the boiling-points observed by Baker were abnormally high because the liquid mixture, before reaching the boiling-point, had already partially evaporated.

A little later,³ Smits pointed out that in the reversible change $\alpha \rightleftharpoons \beta$ the reaction \leftarrow may become stationary sooner than the reverse change \rightarrow in which case a phase should arise containing an excess of the β type of molecule, or this molecular species exclusively; but then it is tacitly assumed that a trace of moisture can displace the inner equilibrium to a very considerable extent, the thermodynamical significance of which is that a very large amount of energy is required to withdraw the last traces of water from a substance. This Smits considered to be not improbable.

He pointed out, however, that there was no definite proof at that time that the equilibrium was not merely fixed at the drying temperature. A small elevation of the boiling-point could have been explained from the circumstance that the fixation temperature was generally considerably below the boiling-point. Similarly, he suggested, in the case of the elevation of the melting-point of sulphur or iodine, the much smaller rises might have been explained by the displacement which the inner equilibrium in the solid phase undergoes with rise of temperature.

Smits also suggested that the question as to whether intensive drying actually changes the inner equilibrium or merely fixes it could be readily answered experimentally. If the vapour pressure of the liquid phase changes solely as a result of intensive drying, this change must take place before any portion of the liquid is distilled off, and thus it is certain that during the drying

¹ *J. Chem. Soc.*, **101**, 2339 (1912).

² *Z. physikal. Chem.*, **100**, 477 (1922).

³ *Theory of Allotropy*, English Edition, 1922, p. 319.

process the inner equilibrium has been displaced. If, however, the vapour pressure remains constant, and a decrease in vapour pressure first appears after a portion of the liquid has been distilled off, intensive drying then acts merely by fixing the inner equilibrium state. He suggested that the same question could also be settled by determination of the boiling-point, if the boiling-point were observed when the intensively dried liquid was boiled under a reflux condenser and the volume of the vapour kept small. If fixation only occurred, the boiling-point would not change, but if part of the liquid were distilled off, the boiling-point would then immediately rise. If, however, the inner equilibrium were also displaced, the boiling-point would change before any liquid were distilled off. He leant towards the latter view. This was confirmed by Mali in 1925, and about the same time by Smits himself.

Discussing this equilibrium shift from the point of view of his theory of allotropy, Smits¹ again took the simple case of a so-called simple substance which exists in two molecular species α and β . For such a case, three different possibilities may be considered:—

A. It is possible that both α and β are more stable in the moist state than in the intensively dried state. In this case we obtain two curves for the values of the thermodynamic potential as a function of the composition x at constant pressure and temperature, one corresponding with the moist and the other with the intensively dried substance. The curve for the more stable, moist mixture will have a lower value, as indicated in Fig. 17. Since the inner equilibrium is always situated at the minimum point, (1) it must be quite fortuitous if the compositions of the dry and moist inner equilibria were the same, and (2) the composition of the dry inner equilibrium may be situated either to the left or to the right of that of the moist inner equilibrium.

B. Another possibility is that the α -form is stable in the moist and the β -form in the intensively dried state. In this case we obtain Fig. 18, and the conclusions are the same as in the first case.

C. Finally we have the possibility that the intensive drying has no influence at all on the stability of the pseudo-components. It is evident that in this case the $\xi - x$ curves for the intensively dry and the moist mixtures coincide completely, and consequently the compositions of the dry and moist inner equilibria are also identical.

¹ *J. Chem. Soc.*, 1926, 2655.

From these considerations, Smits deduced that, if intensive drying has any influence on the stability of the pseudo-components, we may, in general, expect a displacement of the inner equilibrium by intensively drying a substance, but the direction of this displacement cannot be predicted. Thus the inner equilibrium may be shifted by intensive drying in one case in the direction of the more volatile pseudo-component α , and in another case in that of the less volatile pseudo-component β . In the limiting case, this displacement may take place practically along the axis of one of the pseudo-components.

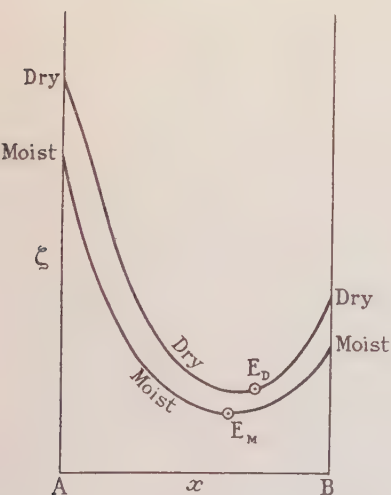


FIG. 17.

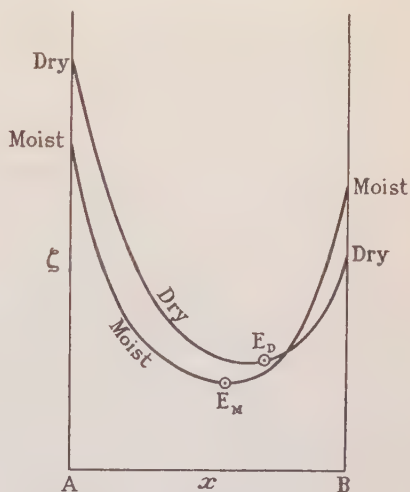
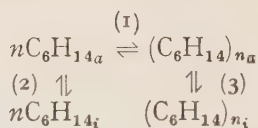


FIG. 18.

A picture of the mechanism whereby the inner equilibrium in a system can become shifted and frozen by intensive drying has been given recently by Smits.¹ This is developed from his earlier explanation of the reason for the loss of activity by molecules on drying, viz. that the latter process causes a shift in the inner equilibrium between active and inactive molecules towards the inactive side. Now in the case of a system such as hexane, it is assumed that it is possible that an equilibrium exists between the active and inactive molecules of the same kind, and also between the active members of different kinds. A direct transformation between the inactive molecules of a different kind is considered to be impossible. Only after having taken up

¹ *Chem. Weekblad*, **25**, 82 (1928).

activation energy are these molecules supposed to be able to react, so that only in an indirect way can a transformation between the inactive molecules of different kinds take place.



Now it is supposed that by increasing the degree of dryness the velocity of these transformations is decreased, and finally they are stopped completely, owing to the shifting of the equilibrium between the active and inactive molecules of the same kind towards the inactive side. If these shifts keep step together, a mixture of the inactive molecules of the different kinds is obtained having a composition equal to the composition in bulk of the moist system. If, however, these shifts do not keep step, a mixture will be obtained of the inactive molecules of the different kinds, the composition of which will differ from the composition in bulk of the original substance. It is supposed that a change in the vapour pressure at the drying temperature proves a change in the composition. If active and inactive molecules are thermodynamically equal, the change in vapour pressure must be effected by the change in the bulk composition. In the other case a change of the vapour pressure will be caused completely or partially by the change in concentration of the active and inactive molecules of the same kind.

Further, Smits shows that in the simplest case the inner equilibrium may be an equilibrium between two kinds of molecules, one active and the other inactive, and both of the same size. If they are not of the same size the other representation must hold. Also in this simple case the final substance will not be a mixture but a real simple substance. Smits does not consider that any examples have been so far investigated which show this simple character, however.

Smits also points out that the activating influence of extremely small traces of water is not so mysterious as would appear at first sight, since the fraction of the total number of molecules existing in the active state is only of the order of magnitude of 10^{-10} , and experiments make it probable that the fraction of water molecules necessary for the activation of a completely inactive system is of the same order of magnitude as this concentration of the active molecules formed by activation.

G. N. Lewis' Theory.—Much the same views as those of Smits were also put forward by Lewis.¹ However he disagreed with Smits' conclusion that a large shift of the inner equilibrium is thermodynamically possible, and is, in fact, the explanation of the phenomena observed by Baker. He pointed out that little, besides the Laws of Thermodynamics, is required to prove Raoult's Law for infinite dilution, but that Smits' hypothesis seems to imply changes in the activity of the solvent which are thousands of millions of times as great as those demanded by Raoult's Law. Hence he concluded that the mere removal of the last traces of water from a system could not appreciably change the existing equilibrium between the several molecular species; and if the water acts as a catalyst for the process of interchange between one molecular species and another, its removal could only serve to "freeze" the existing states of equilibrium, by inhibiting further interchange between the various forms. This he compared with the action of ammonia as a catalyst in the interchange between the two molecular species in liquid sulphur. In the absence of ammonia, the change from one species to the other is inhibited and the sulphur behaves as a mixture, e.g. it has a freezing range of temperature. Lewis explained Baker's results by supposing a liquid to consist of a mixture of molecules A and B, and its vapour solely of the simpler molecules A, all in equilibrium with one another. Then, imagining that the removal of the last trace of water or other catalyst inhibits the reaction between A and B in either direction; if this should be done at constant temperature, the vapour pressure will be the same as before, as well as the proportions of A and B in the liquid. But, if the liquid is heated, more of the A molecules will escape into the vapour phase, and eventually the liquid will consist of molecules B almost entirely. In order to boil this liquid, a temperature must be attained at which either the B molecules themselves vaporise or the rate of formation of A from B, in spite of the absence of any catalyst, is rendered appreciable by the increase in temperature. It was suggested that both processes occur simultaneously. This theory was claimed to be in accordance with the experimental data available at that time.

Lewis also predicted that on condensing a dried dissociated vapour, a liquid would be obtained which would have a lower boiling-point than the normal liquid.

The several molecular species which were supposed to exist in the liquid were likened to the complexes produced during

¹ *J. Amer. Chem. Soc.*, **45**, 2836 (1923).

crystallisation. Assuming the equilibrium between these to be frozen only, it would be expected that static properties should remain the same after drying. This had been confirmed by Baker in the case of volume. Surface tension, as measured by the capillary rise method, gives rise to a process analogous to the formation of a new phase, so Lewis concluded that the surface tension may be altered by the drying. The change in colour of nitrogen trioxide was attributed to either the colouring power of water, or to the absorption of light giving rise to a chemical process not occurring in the absence of a catalyst.

The elevation of the freezing-point, according to this theory, might be due to the ease of crystallisation into space lattice, simple molecules fitting more readily than the more complex. As simple molecules crystallise, he suggested, the freezing-point should drop, and fall below that of the undried liquid.

Lewis pointed out that if it were found that circulation of a liquid through phosphorus pentoxide gave different results from standing over the pentoxide, and if static properties were altered it would be necessary to assume that a liquid is not generally in its most stable state, but tends to become more complex (cf. the tendency of precipitates to form a single crystal); and the original state could only be restored by some agitation to give the necessary energy to convert it into the less stable state.

Mali's Theory.—S. B. Mali¹ explains the behaviour of water in the transformation of binary mixtures of moist liquids on Baly's theory of residual affinities. Since the possession of residual affinity tends to endow a compound with the power of forming addition compounds with other substances, the existence of residual affinity is accompanied by the existence of force lines in the surrounding æther. Every group of atoms must have round it a field of force whose magnitude must depend on the amount of residual affinity present. As a consequence, there must be a certain amount of condensation of the lines of force of the various atom groups, and the system will be more or less closed. If these closed systems receive suitable energies, they may open again. The presence of a third substance may serve to open these compounds so that they will be capable of free existence and also will be free to take part in chemical reactions. This third substance can open the compounds by itself absorbing radiations selectively (probably in an excited state), and emitting them again in the space occupied by the compounds. It thus plays the rôle of a catalytic agent.

¹ *Phil. Mag.* (vii.), 5, 609 (1928).

Mali supposes that the simple unassociated molecules of a dry liquid do ordinarily form compounds among themselves on account of their residual affinities. But in the presence of moisture these molecules are energised by radiations selectively absorbed and radiated by water molecules, and are capable of independent existence as individual molecules. The amount of radiation from the water molecules which energises the closed molecular systems of the moist liquid must be a function of temperature, and it is expected to increase with temperature. On this theory we expect that at very low temperatures most of the molecules of a moist liquid will behave as closed systems, i.e. there will be little or no difference between a moist and a dry liquid at very low temperatures according to this theory.

Smits' Earlier Experiments.—In order to confirm his theoretical predictions, and thence to lend support to his theory of allotropy, a series of experiments were started in a methodical manner by A. Smits and his collaborators in 1923, and these have been continued right up to the present time. These researches will be described in more detail in later chapters, so only a slight indication of the development of the subject can be given here.

Baker's experiments on the change of the boiling-point of benzene with intensive drying were first repeated. It was shown¹ that the boiling-point increased progressively with drying over a period of nine months. At the end of this time, the temperature of the liquid at the boiling-point was 87° and that in the vapour rose to 85° C. A crack then developed, and although it was sealed immediately, the effect disappeared almost completely in a month.

Two self-drying systems were next investigated. The case of sulphur trioxide² was particularly interesting because definite fractionation was carried out. The vapour pressure curve became progressively lower as fractions were removed, and modifications were obtainable in a pure state which could not be obtained when there was a small amount of moisture present. Phosphorus pentoxide was investigated in a similar manner.³

Mali's Investigations.—S. B. Mali⁴ dried four liquids, carbon tetrachloride, benzene, carbon disulphide, and toluene, for four months. The type of apparatus he employed is shown in Fig. 19. The liquid was contained in the tube *AB*, which was connected to two side tubes, one of which was attached to the phosphorus

¹ Smits, *J. Chem. Soc.*, **125**, 1069 (1924).

² Smits and Schoenmakers, *ibid.*, **125**, 2554 (1924); 1926, 1108.

³ Smits and Rutgers, *J. Chem. Soc.*, **125**, 2573, (1924).

⁴ *Z. anorgan. Chem.*, **149**, 150 (1925).

pentoxide tube *P*. The other passed to a *U*-shaped mercury manometer, *M*, of which the further limb passed to a tap *S* lubricated with Baly's vacuum grease. Pure mercury was introduced into this tube through the side tube *R*, which was then sealed off. Before the pentoxide tube was added, the apparatus was cleaned with bichromate solution, washed, and dried by evacuation, the whole being finally heated whilst evacuated so that all the moisture was removed. The pentoxide tube was then added, and mercury placed in the manometer. The liquid to be examined was introduced into *BC*, and the apparatus immersed in ice and salt. *AB* and the further limb of the *U*-tube

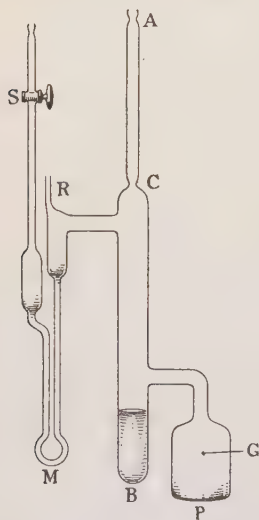


FIG. 19.

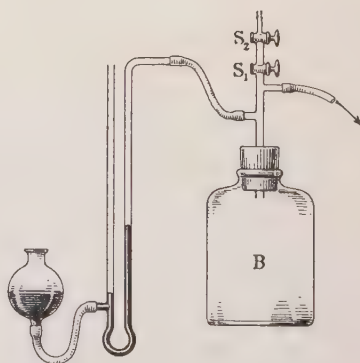


FIG. 20.

were connected to a vacuum pump, avoiding any entry of mercury into *BC*. The liquid was not vaporised to any extent whilst immersed in the cold mixture. When all the apparatus was evacuated, the tube was sealed at *C*, and the tap *S* closed. Drying was carried out in two different series, at ordinary temperatures (*circa* 27° C.), and at 43° in a thermostat.

The vapour pressures were determined by means of the apparatus shown in Fig. 20. Between the two manometers was a large flask *B*, which could be connected with an oil pump through the capillary tube between the taps *S*₁ and *S*₂, so that the pressure could be very slightly adjusted. During the observations the barometric height was noted, and also the mercury

level in both limbs of both manometers, and hence the vapour pressure of the liquid at the temperature determined. Drying was carried out from May to September, 1925. It was then found that in each case the vapour pressure of the liquid at the drying temperature had diminished with drying. Hence he concluded that the intensive drying not only fixed the inner condition of liquids but also displaced their inner equilibria. A rise of temperature was also found to accelerate the drying of the liquids, since more effect was observed with the liquids which had been dried at 43° C. than with the specimens dried at room temperature. From this fact Mali suggested that the pseudo-form of the liquid, the presence of which accounts for the lowering of the vapour pressure and the surface tension change, is according to the Le Chatelier and Braun Principle of Mobile Equilibrium, formed with absorption of heat. The refractive index of benzene also changed slightly on drying.

Modern Types of Intensive Drying Apparatus.—As several general types of intensive drying apparatus have been devised by Smits during the last few years, it may be convenient to describe them together here. They may be divided broadly into two classes, those employing a glass spring pressure gauge, and the other types in which a mercury indicator is used. A few years ago it was thought that the presence of mercury would be detrimental in an intensive drying apparatus, but it has now been shown that if the mercury be dried and other precautions taken, they may be adopted quite safely. The glass gauge type, however, is still useful, especially for liquids which attack mercury. In most of the recent work the glass has been specially prepared with a view to removing any capillaries in the walls of the tubing, which may be open on the inside and so occlude moisture. For this purpose the glass tubes are drawn out at one end, the capillaries at the sealed end thus being removed by fusion. The capillaries running along the wall of the tube are then removed by heating the tube slowly from the drawn off end to fusion point. It has been shown that liquids may be intensively dried much more rapidly in an apparatus constructed of glass prepared in this manner than if the glass is unprepared.

Storage Apparatus.—A convenient form of storage apparatus described by Smits is of the form shown in Fig. 21. From this type of apparatus specimens of liquids which have been subjected to a fairly thorough preliminary drying may be readily distilled into the drying apparatus. Before the vessel *B* is charged with this substance, phosphorus pentoxide is distilled into vessel *A*. Tube *p* is therefore sealed to the distilling tube so that pure

phosphorus pentoxide can be distilled in a current of dried oxygen, whilst tube *q* is sealed off and *t* is connected to a *U*-tube containing

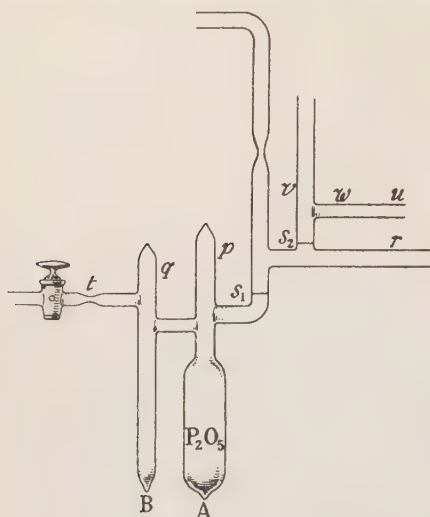


FIG. 21.

phosphorus pentoxide and a wash-bottle of sulphuric acid. Pure phosphorus pentoxide is first distilled into vessel *A*, tube *q* opened, and vessel *B* filled with the substance to be studied, whilst a current of oxygen escapes by *q*, tube *t* being closed temporarily. After cooling *B* in a mixture of alcohol and solid carbon dioxide or in liquid air, *q* and *p* are sealed off successively and *t* is connected with the high vacuum pump. When a high vacuum is reached, the capillary of tube *t* is sealed off. The substance in *B* is now distilled on to the phosphorus pentoxide in *A* and the storage apparatus is ready.

Glass Spring Indicator Types.—The first type of drying apparatus employing a glass spring indicator pressure gauge was of the type shown in Fig. 22. This is filled in the following

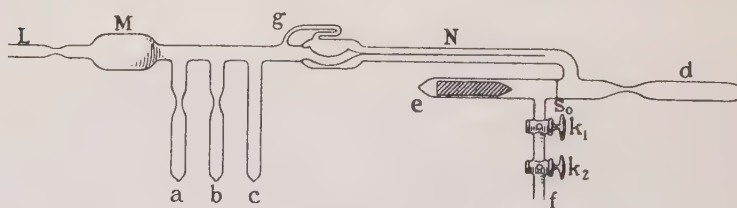


FIG. 22.

way: Vessel *M* is sealed to the phosphorus pentoxide distilling tube, and tube *d* to the tube *r* of the storage apparatus. After heating the tubes, vessels, and breaker in a current of dried oxygen, the capillary ends of the tubes *a*, *b*, and *c* are sealed off successively, and finally the oxygen leaves the apparatus by way of the breaker tube *v*, connected to a *U*-tube with phosphorus pentoxide and a wash-bottle containing sulphuric acid. Pure

phosphorus pentoxide is now distilled into the vessel *M*, *L* is sealed off, and the tube *v* connected to the mercury diffusion pump. When a high vacuum is reached, *v* is sealed off. The septum *S*₁ is now broken by shaking the apparatus, and a small quantity of the previously dried substance is distilled into tube *C* by cooling the latter. After sealing off tube *d*, the vapour pressure apparatus is set up rigidly, *M* cooled in liquid air, the connection between the mantle of the glass spring and the vessel *M* broken by sealing off the capillary tube *g*, and the zero position of the needle of the glass spring fixed. Subsequently the tube *e*, with septum *S*₀ is also evacuated, the two taps *k*₁ and *k*₂ are closed, and the septum is broken by shaking the apparatus. In this way that part of the apparatus containing the substance to be studied is never in connection with the taps, and consequently is completely free from the vapour of the tap grease. After determination of the vapour pressure at a series of suitable temperatures, the liquid is distilled on to the phosphorus pentoxide and the apparatus put aside for drying to proceed.

To study the effect of distillation on the vapour pressure of intensively dried substances, it is necessary that an apparatus of this type should be provided with several tubes with capillaries.

After a portion of the substance has been condensed in such a tube, the capillary can be sealed off and the vapour pressure determined again. The difficulty here is that the process of intensive drying in an apparatus containing capillaries will require a much longer time than in an apparatus with very wide tubes.

This drawback is somewhat overcome in the second, newer type of spring indicator apparatus, which is of the form shown in Fig. 23. As wide tubes in general are considered favourable for achieving rapid intensive drying, this form of apparatus is made of tubing of 25 mm. internal diameter. It contains one or

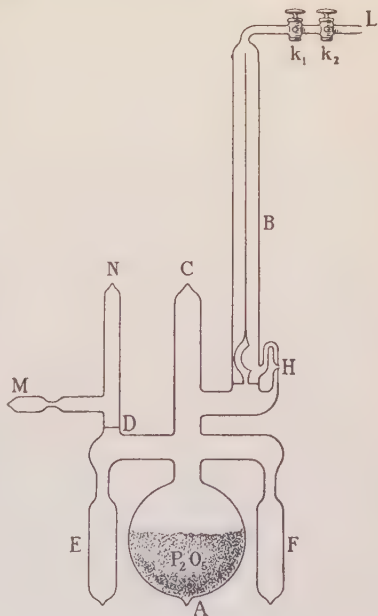


FIG. 23.

more condensation tubes, but without any constrictions. The condensation tubes are connected to the apparatus by tubes about 10 mm. wide, which can be sealed off successfully *in vacuo* by a skilled glassblower.

Mercury Indicator Types.—The first mercury indicator type of apparatus devised by Smits is shown in Fig. 24. This is filled as follows: Bulb *A* is filled with fine distilled phosphorus pentoxide from a storage vessel, and the tube sealed off while a strong current of dried nitrogen is passing through in the opposite direction. Bulb *B* is then filled in the same way with the substance to be studied and, after cooling this bulb, its tube is sealed off as short as possible. Subsequently, bulb *G* is filled with about

10 c.c. of pure dried mercury and sealed. Tube *L* is connected to the high vacuum pump whilst *B* is cooled in a bath of alcohol and solid carbon dioxide or in liquid air, and bulb *A* is heated in a water bath at 80°. In the meantime the mercury is heated to drive out dissolved air. After closing tap *k*, the substance in bulb *B* is heated, to fusion if possible, and then cooled again. Cock *k* is then opened and the apparatus evacuated again. This process is repeated three times.

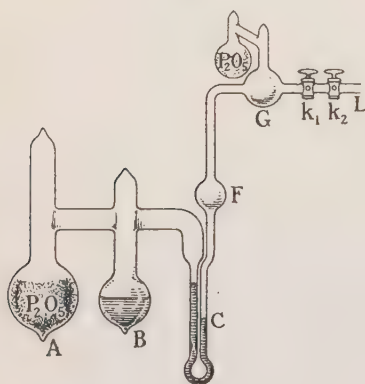


FIG. 24.

Finally, cock *k* is closed again and the connection to the high vacuum pump broken. The tubes *C* are filled with mercury by inclining the apparatus, which is now ready. The mercury manometer is here used just in the same manner as the glass spring gauge. This type of apparatus is made of tubes of 25 mm. diameter, and the quantity of phosphorus pentoxide is very large in proportion to the quantity of the substance to be dried.

With an apparatus of this type, capillaries are not necessary, for should it be desired to distil off a portion, it may be done quite easily in the following way. The pressure difference between the left- and right-hand side of the mercury indicator is raised to such a degree that the mercury is pressed up slowly into bulb *F* and vapour bubbles through it. When a sufficient quantity of the substance has been distilled off in this way, the mercury is passed back again into the U-tube *C* and the vapour pressure determined.

With the object of accelerating the drying process, this type of apparatus has been modified as shown in Fig. 25. In this apparatus a circulation method is used, and is especially useful in the case of liquids. This circulation is caused by cooling the inner tube of the double-walled vessel *C* by means of a current of tap-water. Since the whole apparatus is placed in a bath of 45° , the vapour of the liquid is condensed on the outer wall of the inner tube of *C* and the condensed liquid drops into tube *D*, through which the liquid runs into the wide vessel *A*. Here the liquid is evaporated again, and after passing through the wide *U*-tubes filled with

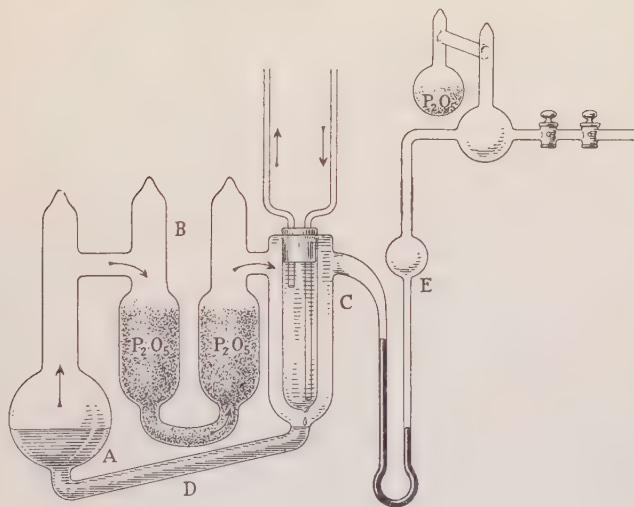


FIG. 25.

very fine pure phosphorus pentoxide, the vapour is again condensed in *C*, and so on.

In order to determine the vapour pressure of a fraction distilled off from the dry liquid, an apparatus is used of the form shown in Fig. 26. Since this type contains a large amount of mercury in the manometer *C*, the period of drying required is much longer than in the other forms of apparatus. When it is desired to remove a fraction, the bulb *B* is placed in a bath at 0° C., whilst the remainder of the apparatus is at room temperature. As soon as the liquid in *B* is condensed, the bath round *B* is removed, and placed round *B'*. The liquid distils slowly from *B* to *B'*, and when half has distilled over, *B* is also immersed in an ice bath. Dry air is now admitted by taps M_2 and M_1 , till it drives the mercury in *D* into the limbs of the manometer *C*,

so as to separate the compound into parts, in *B* and *B'* respectively. The apparatus is immediately placed in a large thermostat at any required temperature, and at intervals the vapour pressure difference between the distilled off fraction and the residue can be measured by the manometer *C*, and the vapour pressure of the residue by the manometer *P*.

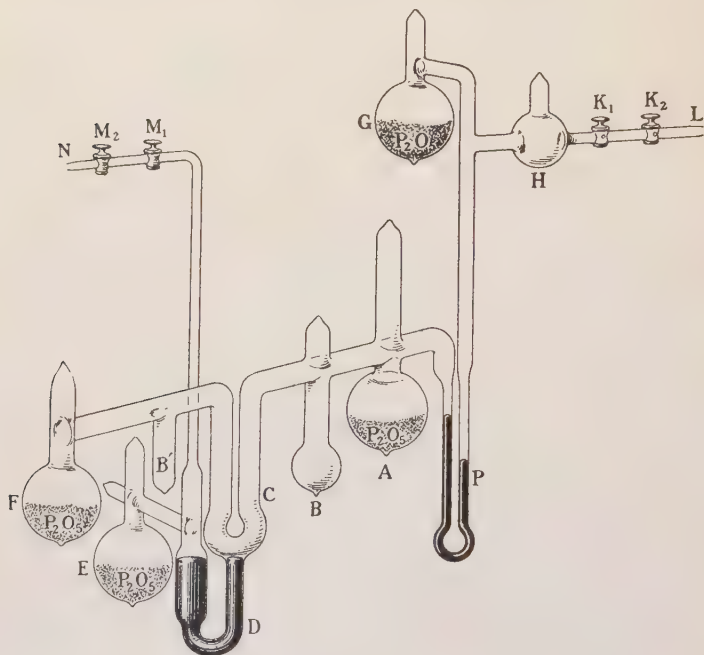


FIG. 26.

Smits' Recent Experiments.—Using the various types of apparatus which have been described, Smits has investigated the influence of intensive drying on a series of liquids of different types. The first of this new series of investigations was the case of nitrogen tetroxide,¹ which was of particular interest because it was the first occasion upon which an increase in vapour pressure, corresponding to a lowering of the boiling-point, was found. This was observed simultaneously by the present author.² In the case of hexane¹ it was shown that when the dried liquid was fractionated, a distillate was obtained with a higher vapour pressure and a residue with a lower vapour pressure than that

¹ *J. Chem. Soc.*, 1926, 2663.

² Smith, *ibid.*, 1927, 867.

of the dried liquid. On standing, however, both these vapour pressures tended to return to the value shown before fractionation.

That phosphorus pentoxide does not react with the liquids causing this effect has been shown by Smits as follows.¹ The liquids were sealed in pieces of apparatus of the type shown in Fig. 22, which contained condensation tubes with capillaries. After two years, the liquids in these apparati did not show the slightest drying effect, the vapour pressure remaining unchanged and on fractional distillation left the same vapour pressure. This was attributed to the slow diffusion of gases, and hence also of moisture, through the capillary tubes. All the latter except one were therefore removed from each piece of apparatus, after which the results shown in Table XXIX. were obtained. The changes in vapour pressure at the drying temperature indicate that the inner equilibrium must be shifted by drying. It is noteworthy that, besides nitrogen tetroxide, both ethyl bromide and bromine have their vapour pressure raised by drying. Hence it appears quite certain that, as predicted by Smits, the inner equilibrium may be shifted in either direction by intensive drying, and the fact that Baker invariably obtained a rise in boiling-point was due to a fractionation effect in a liquid in which the internal changes were very much slowed down.

TABLE XXIX.

Liquid.	Drying Temp. ° C.	Duration of Drying (months).	Temp. ° C.	Vapour Pressure (cm. Hg).		
				Dry.	Moist.	Change.
<i>n</i> -Hexane . . .	20-23	29	22.80	12.75	14.00	- 1.25
Carbon disulphide . .	"	26	20.55	29.56	30.86	- 1.30
Ethyl bromide . . .	"	26	22.90	44.85	43.40	1.45
Bromine	"	35	21.14	19.47	18.38	1.09
Nitrogen tetroxide . .	"	16	22.90	85.40	82.10	3.30

Finally, Smits has also carried out preliminary experiments on the change of the vapour pressure of mercury on drying. These show a slight change, which, however, disappears at about 300° C., although heating to such a temperature does not cause the vapour pressure at low temperatures to exhibit afterwards their normal values, hence this is not due to moisture coming off the walls of the vessel. The conclusion drawn is that the

¹ *Z. physikal. Chem.*, **129**, 33 (1927).

degree of drying effective in causing the attainment of the inner equilibrium to become slow at lower temperatures is insufficient at higher temperatures.¹

The great importance of this observation seems to lie in the fact that the behaviour is almost perfectly analogous to that of dried ammonium chloride. As was mentioned in Chapter VII., the vapour pressure of this compound when dried is lower than that of the moist substance at lower temperatures, but at higher temperatures the two vapour pressure curves converge and eventually become identical. In both cases the curves are quite reproducible, and the values obtained can be reached from either direction. Hence this more than ever accentuates the fact that the ammonium chloride case can be regarded as the connecting link between the observations made on the influence of intensive drying on the progress of chemical reactions and on its effect on physical properties. In both the cases of mercury and of ammonium chloride the vapour pressure at lower temperatures is diminished by drying, but whereas in the case of mercury this effect is attributed to a change in the inner equilibrium, with the ammonium chloride the shift in the equilibrium must be concerned both with the inner equilibrium between the different forms of ammonium chloride, and also with the ordinary chemical equilibrium between these and the dissociation products, ammonia and hydrogen chloride. It would appear that at high temperatures these equilibria remain "normal" even in the presence of only a very little water vapour.

Smits' Criticisms of Baker's Observations.—A severe attack on the methods employed by Baker to prove the greater complexity of dry liquids than of moist has recently been published by Smits.² He pointed out that the changes in vapour pressure at constant temperature and without distillation which have been found after several years' drying, are relatively very small. On the other hand, Baker's experiments which furnished abnormally high vapour densities seemed to contradict these results. Smits considers it unlikely that the carefully purified liquids dried for two to five years with a relatively large quantity of phosphorus pentoxide would be less completely dried than Baker's. Since the studies of "velocity phenomena," e.g. rapid distillation and rapid heating, showed rather large effects, whilst "equilibrium phenomena," e.g. vapour pressure, revealed little or no effect, it was suggested that the anomaly would disappear if it could

¹ *Chem. Weekblad*, **25**, 82 (1928).

² *J. Chem. Soc.*, 1928, 2399.

be proved that the properties studied by Baker were actually all velocity phenomena.

In the case of Baker's *vapour density* determinations, e.g. with nitrogen tetroxide, the $P - x$ diagram of the pseudo-system at the temperature at which the experiment is carried out is shown in Fig. 27. Supposing that the coexisting phases are L and G , present in inner equilibrium if the little bulb used in Victor Meyer's method is filled with moist nitrogen tetroxide. Let the line $p_1 p_1$ correspond with a pressure of one atmosphere. If a bulb is broken, the liquid evaporates, but the evaporation is accompanied by a chemical transformation $N_2O_4 \rightarrow 2NO_2$, and the unsaturated vapour formed is given by the point G_1 lying on the vapour curve GG_0 of the unary figure, so that the composition of

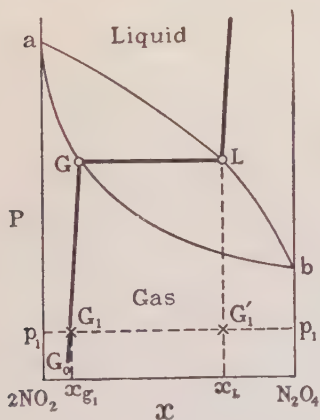


FIG. 27.

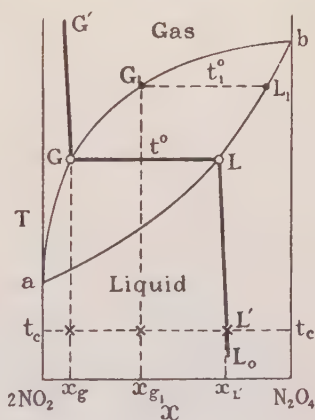


FIG. 28.

the vapour formed is not x_L but x_{G_1} , and it is to this composition that the vapour density found corresponds.

If, however, the nitrogen tetroxide is so intensively dried that, although the inner equilibrium is not yet fixed, the inner transformations are distinctly retarded, the result of the vapour density determination will now be quite different, and when a bulb is broken the liquid will behave to some extent as a mixture. Supposing that the liquid behaves as a real mixture, in this case the reaction $N_2O_4 \rightarrow 2NO_2$ will not take place, and if all the liquid is evaporated, a gas phase G_1' will be formed, the composition of which is equal to the composition of the liquid before the bulb was broken. Hence the vapour density found will correspond with the composition x_L . If, however, the inner equilibrium is not yet fixed but the inner transformations are only retarded,

the composition of the gas phase, at the moment of the reading, will be given by a point between G_1 and G_1' ; hence in this case the vapour density will show an abnormally high value, notwithstanding that the inner transformations are not yet stopped, but only retarded. If it had been possible to wait till the inner equilibrium were attained, the ordinary vapour density would have been found, but in this method readings have to be taken rapidly before diffusion of the vapour occurs into the air column.

Thus Smits concluded that vapour density determinations give values corresponding to a velocity phenomenon and indicate large changes in the vapour density, since it enables us to find temporary changes due to the non-attainment of inner equilibrium. The vapour pressure of the same dried liquid, at constant temperature, is still completely unchanged, however, being an equilibrium phenomenon.

Similarly it is shown that the determination of the *latent heat* of vaporisation or condensation is the determination of the effect of a velocity phenomenon, and it is suggested that it appears to be one of the best methods of finding out whether retardation of the inner equilibrium has already occurred. Considering a $T - x$ diagram for constant pressure, say one atmosphere (Fig. 28). In the pseudo-diagram the unary figure is given by the curves L_0L and GG' and the horizontal line GL ; hence L and G are coexisting liquid and gas phases at the boiling-point.

Supposing now that the heat of condensation is determined and the temperature of the calorimeter corresponds with the line t_0t_0 , two cases may be discussed. (1) If the substance behaves in a unary manner, the vapour phase G will be transformed into the liquid phase L' lying on the curve LL_0 , and the heat of condensation therefore contains an exothermic heat of reaction corresponding with the change of composition from x_g to $x_{L'}$. (2) If, however, the substance has become slow by intensive drying, and therefore behaves to some extent as a mixture, the point representing the boiling liquid will move along the curve Lb and that of the vapour phase along the curve Gb in such a way that the coexisting phases always lie on the same horizontal line—if the boiling-point is increased, for instance, from t_0 to t_1^0 the coexisting phases are L_1 and G_1 . Now it is evident that the condensation of the vapour phase G_1 in the calorimeter will give rise to a smaller heat of condensation, since the composition of this vapour phase x_{g_1} is nearer to $x_{L'}$ than is x_g , so that although the composition of the condensed vapours lies between x_g and x_{g_1} , the exothermal chemical reaction is smaller than in the first case.

In connection with Baker's *boiling-point* determinations he pointed out that the inner equilibrium cannot have been fixed, because if such were the case a distillate with an abnormally low boiling-point would have been formed, whereas Baker's experiments show that the opposite occurred, the distilled off portion boiling at the same temperature as the residue; hence the inner equilibrium must after some time be re-established in the distillate, which will then show the same behaviour as the initial liquid. Also, in spite of contact with moist air, the liquids must have been still slow.

The low *vapour pressure* found by Baker for ether (374 mm. at 20° instead of 442 mm.) was also supposed to be completely in agreement with a slow establishment of the inner equilibrium. In Fig. 29, the molecular volume V is plotted against the composition x (expressed, for example, in mols.) per cent. The temperature considered is that at which the vapour pressure determination is carried out. At this temperature, a is the volume of n gram-mols. of pure liquid $(\text{C}_2\text{H}_5)_2\text{O}$, i.e. liquid consisting only of the first pseudo-component or the completely dissociated second pseudo-component, under its own vapour pressure, and c is the volume of n gram-mols. of gaseous $(\text{C}_2\text{H}_5)_2\text{O}$ in equilibrium with this liquid phase. Points b and d have the same significance with regard to 1 gram-mol. of the second pseudo-component $[(\text{C}_2\text{H}_5)_2\text{O}]_n$. The vapour pressure of the pure liquid $(\text{C}_2\text{H}_5)_2\text{O}$ will be much larger than that of pure liquid $[(\text{C}_2\text{H}_5)_2\text{O}]_n$, and the molecular volume of the coexisting vapour is therefore much smaller than that of the vapour coexisting with the latter liquid. In Fig. 29 it is supposed that the difference is so large that n times the molecular volume of the vapour coexisting with liquid $(\text{C}_2\text{H}_5)_2\text{O}$ is even smaller than the molecular volume of the vapour coexisting with liquid $[(\text{C}_2\text{H}_5)_2\text{O}]_n$. This is possible, but not essential. The line ab gives the molecular volumes of the liquid mixtures, whilst cd gives the molecular volumes of the gaseous mixtures of the pseudo-system. If the system behaves in a unary manner, only one liquid and one vapour coexist, viz. those

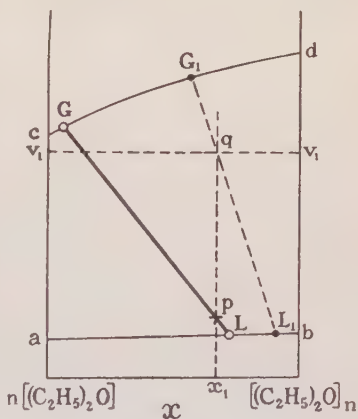


FIG. 29.

given by G and L corresponding to a definite pressure—the vapour pressure of the liquid in inner equilibrium. It may readily be seen that the liquid phase is rich in the polymeric, or complex molecules, whilst the vapour phase is rich in the single molecules.

If, now, the bulb containing the dried ether were nearly completely filled, i.e. the volume of the vapour, was relatively very small, the state of the system must be represented by a point on the line LG and quite near to L , so that the total composition corresponds with x_1 . After the bulb is broken the system attains a relatively large volume, given, say, by v_1 . Hence if in the first moments the substance behaves as a mixture owing to its sluggishness caused by drying, point q on the nodal line L_1G_1 will give the state of the mixture, and from the position of this point we see that the quantities of the coexisting phases are largely changed, the ratio having become G_1q/L_1q instead of Gp/Lp . This nodal line is situated in the region of lower pressures, so that the vapour pressure will be abnormally low but will increase slowly. Similar effects must have accounted for Prof. and Mrs. Baker's results with nitrogen trioxide and nitrogen tetroxide.

Similarly the fact that Baker found that the surface tension and boiling-point of benzene was changed on application of an electric field (see p. 218) shows that *surface tension*, though not a velocity phenomenon, is not a trustworthy criterion of the internal complexity of the liquid. The change in boiling-point is found only on heating the benzene in an oil bath and is not accompanied by a change of vapour pressure. It now appears to be merely a superheating phenomenon; hence it seems most probable that, if a liquid by long standing in a sealed tube has become free from dust particles, the surface tension may be changed, and is therefore no longer a trustworthy criterion of the state of the inner equilibrium.

Various Recent Investigations.—Certain series of experiments have been reported recently in which liquids have been intensively dried for long periods over phosphorus pentoxide, but no abnormalities in physical properties could be observed after this period. Lenher and Daniels¹ have reported that both benzene and carbon tetrachloride have been dried in capillary-free hard-glass tubes for four years, but the boiling-point was unaltered. The boiling-point measurements were made in two ways; (a) the tube was opened at one end and put in a bath of

¹ *Proc. Nat. Acad. Sci.*, 14, 606 (1928).

sulphuric acid, the temperature of which was raised slowly, the temperature of both liquid and vapour when ebullition commenced being noted; and (b) the liquid was heated internally by a platinum wire heating element sealed through the glass, about 5 c.c. of the dried liquid being decanted into the apparatus for a determination. In every case the drying tube was opened directly to the air, it being concluded from Baker's results that the recovery of the normal state was not rapid in comparison with the time of measurement (1 hour). With the platinum wire heating apparatus, absolutely normal boiling-points were obtained, but, using the heating bath both liquids could be easily superheated 1.5° before ebullition began.

This phenomenon has now been further studied by Lenher,¹ who finds that a specimen of carbon tetrachloride which had been dried for five years boiled at 76.8°C . at 762.2 mm. (a normal value) when heated with a platinum wire-heating element, but did not boil till the thermometer in the liquid registered 90° when heated in a bath, the boiling being then quite steady. The liquid was not entirely free from dust particles and tiny particles of phosphorus pentoxide. The vapour density of the dry liquid, determined by Victor Meyer's method after introduction in small bulbets, indicated the normal molecular weight. From these results Lenher concludes that superheating was an important factor in Baker's experiments.

Baker's criticism of these results,² however, is that Lenher's liquids were transferred into comparatively moist tubes before the measurements were carried out.

Lenher has also shown³ that undried liquids can exhibit abnormally high boiling-points when the conditions for superheating are ideal; thus benzene could be superheated 26° , carbon tetrachloride 30° , and water 12° . When boiling did begin it was not always violent, but was sometimes quiet and regular. In the case of benzene, the crucial experiment of Baker and Smits (cf. p. 191) could be repeated, the vapour temperature rising steadily as heating was continued till it reached 89.5° (liquid temperature 90°) without the liquid boiling. The conditions favouring this apparent rise in the boiling-point are given as: (a) the use of a heating bath; (b) the immersion of the thermometer bulb in the liquid of which the boiling-point is being measured; (c) allowing the liquid to stand in contact with a flocculent solid such as redistilled phosphorus pentoxide; and

¹ *J. Amer. Chem. Soc.*, **51** (1929).

² *Chem. Soc. Meeting*, June, 1929.

³ *Nature*, **123**, 907 (1929); *J. Physical Chem.*, **33** (1929).

(d) distillation of the liquid into a clean flask before determining the boiling-point, which again tends to free the liquid from dust particles.

In another series of experiments, Briscoe, Peel, and Robinson¹ have found that after drying for periods up to fifteen months, both the density and surface tension of benzene were not sensibly altered, and that head and tail fractions did not differ appreciably from the main liquid. When first brought into contact with phosphorus pentoxide, the benzene increased in density by about one part in 80,000; the view that this was due to solution of the oxide was supported by the observation that the evaporation of the benzene in contact with phosphorus pentoxide invariably left white striæ of residue, which could not be removed by repeated washing with distilled benzene.

On the other hand, we have a report that confirms the previous observations that the refractivity of benzene changes on drying. Manley has found² that the refractivity changed continuously over a period of six months' drying. On plotting refractivity against time the resultant graph showed two distinct portions or limbs, both smooth, but with very different directional values. He concludes that the first portion represents the rate of removal of mechanically admixed water, and the second offers a measure of the rate of withdrawal of water in actual combination with the benzene. Further evidence for the actual existence of a hydrate of benzene was obtained from measurements of the specific volume of benzene in the presence of phosphorus pentoxide. This physical "constant" was found to be dependent on the temperature to which the benzene was exposed immediately before a determination was carried out, it being diminished by preliminary cooling and increased by preliminary heating. This is explained by Manley by supposing that, during crystallisation, combined water is ejected from the benzene and taken up by the phosphorus pentoxide, and secondly, as the temperature is raised, the process of dehydration is reversed, and water is absorbed from the metaphosphoric acid just previously formed. Thus it is supposed that the drying power of anhydrous benzene is, within certain limits of temperature, greater than that of phosphorus pentoxide. Similar experiments with benzene in the absence of phosphorus pentoxide show only very small effects of the same kind. It may be pointed out here, however, that Manley's case for the existence of the benzene hydrate is by no means proved. The fact that the value of the specific volume varies with its preliminary treatment may be merely yet another

¹ *J. Chem. Soc.*, 1929, 368.

² *Nature*, 123, 907 (1929).

example of the slowness with which changes occur in intensively dried systems.

Finally, Riley has shown¹ that the dielectric constant of oxygen remains unaltered during ten months' drying, so he concludes that the action of small traces of water vapour in promoting chemical activity is not to be explained by any change in the structure of the molecule on drying.

Discussion.—Taking a general view of the influence of intensive drying on physical properties, we see that the most definite data we have at present are those of vapour pressure change. The results obtained in this field, unlike the measurements of other physical properties, appear to be definite indications of a change in the internal state of liquids on intensive drying, and seem to be incapable of any simple alternative explanation such as can be put forward in almost all other cases. The most outstanding other fact emerging from this work is that all internal changes, including changes of state, seem to occur only slowly when the substance is very dry. It has been shown many times that, when dry substances are in a state different from their equilibrium state, the vapour pressure is very slow in attaining a constant value, and it will doubtless be shown in the future that other properties show the same slow change. It seems possible to explain this only by supposing that slow internal changes are occurring in the substances during this time. For the same reason, changes of state tend to occur slowly. Thus in the case of the vaporisation of a liquid, the less complex molecules tend to pass into the vapour state first. This leaves a residue containing a greater proportion of the less volatile more complex molecules, which vaporise only slowly and which also pass quite slowly into the less complex forms. Thus an intensively dried liquid distils more slowly than a moist liquid; e.g. it was found by the author that whereas a certain volume of nitrogen tetroxide could be distilled over completely between two bulbs in about three hours when first introduced into a drying apparatus, this time increased as drying progressed, and finally some five hours were required for complete distillation to occur over the same temperature gradient, even though the equilibrium vapour pressure of nitrogen tetroxide is raised by intensive drying. This fact doubtless accounts for the fact that Smith and Menzies came to the conclusion that very dry calomel had no vapour pressure at all.

In the succeeding chapters, some details are given of the behaviour of such dried compounds as have been studied at all extensively.

¹ *J. Chem. Soc.*, 1929, 1026.

CHAPTER XIX.

OXIDES OF NITROGEN.

Nitrogen Trioxide.—The case of nitrogen trioxide is of very special interest, for it was during investigations on this compound that the first definite observation of any change in physical properties upon intensive drying was made. Baker's experiments on nitrogen trioxide¹ were commenced with a view to determining whether the carefully dried compound decomposed in the same manner as when moist, or whether, as in the cases of ammonium chloride and mercurous chloride, this decomposition was completely stopped. As indicated, however, these researches had much further reaching results than had ever been expected, in fact they opened up a totally new field for scientific investigation. On this account, the experiments carried out on the decomposition of nitrogen trioxide have not been described among the chemical reactions in the earlier chapters, but will be dealt with here, in order to show the manner in which this aspect of the subject was developed.

Baker dried his nitrogen trioxide in a tube of about 20 c.c. capacity, to which was sealed a capillary tube of about 0.5 mm. external diameter in which a series of ten small bulbs was blown. The whole apparatus was dried by heating whilst a current of dry air was passed through it. A plug of ignited asbestos was placed in the junction of the capillary and the wide tube, and plugs of redistilled phosphorus pentoxide were introduced. The tube was then closed and allowed to stand for a week to ensure the drying of the internal surface of the glass. The nitrogen trioxide was then distilled and condensed in the tube, which was immersed in a mixture of calcium chloride and ice. When sufficient liquid had been collected, a current of nitric oxide dried by phosphorus pentoxide was bubbled through it for an hour and the tube sealed. When specimens were required, the small bulbs were cooled, liquid distilled over, and by a very fine pointed flame the

¹ *J. Chem. Soc.*, **91**, 1862 (1907).

capillaries between the bulbs were sealed off. The bulbs were washed in distilled water, and dried in a desiccator. Analysis showed the liquid to be pure nitrogen trioxide.

To determine the density of the vapour evolved by evaporation of the liquid, weighed bulbs were broken in a Lunge nitrometer over pure dry mercury. The bulb was broken by pressure with a long glass rod which passed through an india-rubber stopper at the bottom of the nitrometer. The gas had very little effect on the dry mercury. The following results were obtained :—

TABLE XXX.

	Weight of Liquid used.	Time of Drying over P_2O_5 .	Temperature.	Pressure.	Density.
1	0.0645 gram	6 days	15° C.	770 mm.	43.2
2	0.0274 "	27 "	14 "	747 "	43.6
3	0.0514 "	13 "	13 "	768 "	48.6

On addition of concentrated sulphuric acid to the gas, solution occurred so rapidly that the rush of mercury up the tube could not be followed with the eye. Hence the gas did not consist of a mixture of nitrogen peroxide and nitric oxide, which undergo only comparatively slow absorption by sulphuric acid.

More careful vapour density determinations were carried out in the modified form of Victor Meyer's apparatus, as previously used for mercurous chloride (Fig. II). The weighed bulb of liquid was placed at the bottom of the cylindrical bulb of the vapour density apparatus, and the movable glass spoon was used to support a piece of heavy glass rod. On turning the spoon, the rod dropped on to the bulb, thus liberating the liquid. The apparatus was previously dried by heating whilst a current of dry nitrogen was passing through. The sealed tube which formed the stopper of the apparatus contained phosphorus pentoxide, and the exit tube was filled with the same substance. The vapour pressures obtained after various periods of drying were as given in Table XXXI.

Since the density of the undissociated nitrogen trioxide is 38, it was concluded that the gas obtained in these experiments must contain a higher polymeride, probably N_4O_6 corresponding to the analogous oxides of arsenic and phosphorus. The variation in the densities obtained was probably due to the fact that the bulbs used came from eight different preparations, the liquid in which was condensed at different temperatures, and which

was allowed different periods of drying over phosphorus pentoxide.

On the other hand, when a bulb was immersed in a freezing mixture, its capillary broken, left a few seconds, and then sealed again, the vapour density of the "moist" liquid so obtained was 28.2 at 22° C. The density of nitrogen trioxide breaking up into N_2O_4 , NO_2 , and NO at 22° C. is 27.8, so it was concluded that in the presence of a mere trace of moisture, practically complete dissociation of the vapour takes place. This was supported by the observation that the boiling moist liquid soon lost its green colour, leaving a yellow liquid which then disappeared, whilst with the dried liquid there was no change in colour as it boiled away.

TABLE XXXI.

No.	Weight of Liquid.	Time of Drying of V.D. Apparatus.	Temperature °C.	Pressure, mm.	Density.
1	0.0649	23 days	22	768	38.1
2	0.0593	4 "	21	744	38.4
3	0.0241	14 "	22	762	41.5
4	0.0487	6 "	20	735	42.0
5	0.0160	6 "	16	756	42.1
6	0.0902	20 "	18	757	42.8
7	0.0452	6 "	22	745	42.8
8	0.0382	14 "	20	744	49.0
9	0.1034	8 "	18	756	49.3
10	0.0299	28 "	21	742	57.0
11	0.1475	22 "	17	802	59.2
12	0.0493	7 "	18	739	59.8
13	0.0134	33 "	60	615	62.2

Some determinations were made of the molecular weight by the lowering of the freezing-point of purified and dried benzene, in order to find whether at a temperature of 4° C. and in solution the higher polymeride would be in a more concentrated state than in the vapour at higher temperatures. This was found not to be the case. Two bulbs from one preparation were used in the first case, and one from another preparation in the second.

I. (a) 0.1364 g. of liquid in 10.2 g. benzene gave depression 0.8°. M.W. = 83.

(b) 0.0455 g. of liquid in 10.3 g. benzene gave depression 0.26°. M.W. = 83.2.

II. 0.0627 g. of liquid in 10.8 g. benzene gave depression 0.29°. M.W. = 95.

In these experiments, the benzene was dried over distilled phosphorus pentoxide, and care was taken that the thermometer and

the tube were as far as possible dried to the same extent. The dried benzene was quite unaffected by the dried trioxide. After a very short exposure to moist air, the solution lost the green colour, at the same time giving off nitric oxide, with effervescence, leaving a yellow solution of nitrogen peroxide.

In a later series of experiments¹ the boiling-point of the dried trioxide was tested. For this purpose a Jena glass tube was used, about 40 cm. in length and 15 mm. in internal diameter.

Into one end was ground a hollow glass stopper, which opened into a wide tube containing phosphorus pentoxide, this tube being drawn out into a long capillary about 2 mm. in diameter, as shown in Fig. 30. The other end of the Jena tube was drawn out till its internal diameter was about 8 mm., its wall being as thin as was consistent with safety. After drying by heating in a current of air dried by phosphorus pentoxide, a bulb of nitrogen trioxide which had been dried over phosphorus

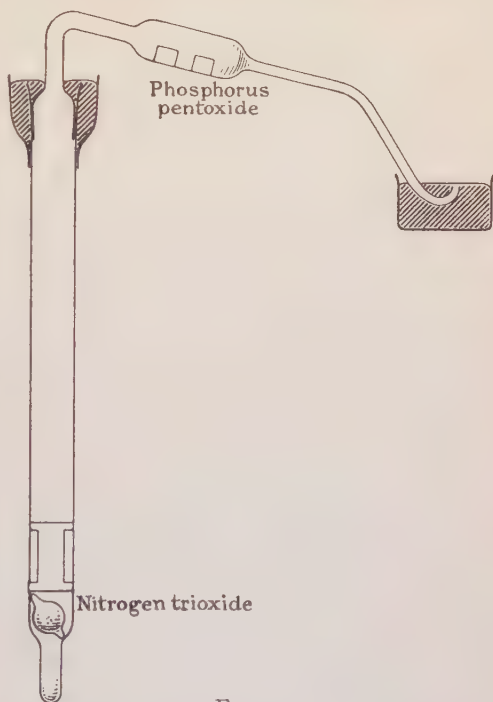


FIG. 30.

pentoxide for three years was introduced. A piece of Jena glass rod was placed above the dried liquid so as to facilitate the fracture of the bulb. The tube was filled with nitrogen dried with phosphorus pentoxide, and kept for three months, the ground joint being protected by a mercury seal. At the end of this time, a thermometer was bound to the thin end of the tube, and the capillary end of the phosphorus pentoxide tube was broken under previously dried mercury. The bulb was broken while the tube was surrounded by melting ice, but no boiling was

¹ Baker and Mrs. Baker, *J. Chem. Soc.*, **101**, 2339 (1912).

perceptible, although the ordinary boiling-point is -2°C . The temperature of the bath was allowed to rise, and the liquid was found not to boil till a temperature of 43°C . was reached. A second experiment indicated a boiling-point of 42.5°C . The vapour of the very dry nitrogen trioxide was red, and on cooling to 10°C . condensed to the green liquid which on further cooling turned bright blue, showing that it was still nitrogen trioxide. On allowing some nitrogen, dried by passage through a long column of phosphorus pentoxide, to enter the tube, the amount of moisture it contained caused rapid dissociation, and the resulting sudden increase of pressure blew the stopper out of the tube.

This abnormal boiling-point was explained on the grounds of a difference of complexity in the liquid. They supposed that a liquid consisting of more complex molecules would have a higher boiling-point than one of simple constitution, and that the almost complete absence of moisture would enable the liquid to boil as such. They considered it probable that a more complex molecule exists in the liquid below -2°C ., since at this temperature a marked change in colour occurs from olive-green to bright blue. A very dry specimen in the possession of Baker, which has been drying since 1907 gradually acquired a blue colour at ordinary temperatures during the earlier years of drying, and has remained blue ever since.

Jones¹ determined the vapour density of dried nitrogen trioxide at a series of temperatures, pressures, and volumes. The results varied from 35.07 at the lowest temperature and volume, to 24.00 at the highest. Complete dissociation into nitric oxide and nitrogen peroxide demands a vapour density of 19, N_2O_3 demands 38, and N_4O_6 76. He considered that the only tenable mechanism for the dissociation was as follows :—

- (a) $\text{N}_4\text{O}_6 \rightleftharpoons \text{N}_2\text{O}_3 + \text{NO}_2 + \text{NO}$ (dry, not further dissociating).
- (b) $\text{NO}_2 + \text{NO}$ (wet, not combining).
- (c) $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ (wet).

Complete dissociation according to (a) gives a vapour density of 25.33. From this he deduced the amounts of "wet" and "dry" material present, and calculated the equilibrium constant of the reaction (a).

Nitrogen Tetroxide.—Among the many reactions which Baker tested in his comparatively early experiments, was the dissocia-

¹ *J. Chem. Soc.*, **105**, 2310 (1914).

tion of nitrogen tetroxide into the dioxide.¹ He heated dry lead nitrate in a dry tube containing phosphorus pentoxide, and condensed the nitrogen tetroxide in a *U*-tube. The colourless liquid became red on warming, and the gas was perceptibly darkened by heating. Hence he concluded that nitrogen tetroxide was dissociated on heating, even when dry.

Baker and Mrs. Baker² tested the boiling-point of dried nitrogen tetroxide in the same manner as that of dried nitrogen trioxide. The amount of the dried liquid available was very small, less than 1 c.c. On raising the temperature of the bath, the liquid was apparently unchanged at 22° C., the ordinary boiling-point. Further heating of the bath produced evaporation, but at 69° the liquid was still visible and not in a state of ebullition. Above this temperature, the liquid, which was orange-red in colour, disappeared. The atmospheric pressure was 757 mm.

The surface tension of dried nitrogen tetroxide has also been determined by Baker.³ The result gave as the multiple of the molecular weight, 3·10 for the liquid containing the drying agent, and 3·00 for that of the liquid alone. He considered that this close agreement was probably to be accounted for by the fact that the liquid in both tubes was distilled from a specimen that had been drying over phosphorus pentoxide for ten years. It was thought that there would have been sufficient moisture left in the tube which was being filled to convert it into the undried liquid, but from this result Baker inferred that this was not the case.

A more complete investigation of the behaviour of this compound when intensively dried was carried out by Smits, de Liefde, Swart, and Claassen.⁴ They used three pieces of apparatus of the type shown in Fig. 22; they were made of Jena glass, in one case capillary-free, with glass spring indicators. The intensive drying took place at room temperature. The results obtained were as follows:—

TABLE XXXII.

APPARATUS I. (Not capillary-free glass.)

Duration of Drying at Room Temperature.	Temperature of Observation, °C.	Pressure of Dried Liquid (cm. Hg).	Pressure of Moist Liquid (cm. Hg).	Drying Effect (cm. Hg).
—	17·70	64·9	64·8	+ 0·1
20 months	20·00	72·9	72·0	+ 0·9
24 „	20·38	75·1	73·35	+ 1·7

[Continued on following page.]

¹ *J. Chem. Soc.*, **65**, 611 (1894).

³ *Ibid.*, **121**, 573 (1922).

² *Ibid.*, **101**, 2341 (1912).

⁴ *Ibid.*, 1926, 2663.

TABLE XXXII.—(continued).

APPARATUS II. (Not capillary-free glass.)

Duration of Drying at Room Temperature.	Temperature of Observation, °C.	Pressure of Dried Liquid (cm. Hg).	Pressure of Moist Liquid (cm. Hg).	Drying Effect (cm. Hg).
$\frac{1}{2}$ month	22.00	78.6	78.9	— 0.3
3 $\frac{1}{2}$ months	17.20	63.55	63.0	+ 0.5
20 ,,	19.80	72.4	71.2	+ 1.2
23 ,,	20.65	76.00	74.1	+ 1.9

On the day the last measurements were made, they determined vapour pressures at temperatures above the drying temperature, with the following results :—

23 months	25.00	92.95	90.6	+ 2.3
23 ,,	30.05	114.95	113.0	+ 1.9

Thus as the temperature rose, the pressure increase passed through a maximum. A quarter of the liquid was now distilled off into one of the tubes, and after sealing this off, the vapour pressure was determined again at the drying temperature, with the following result :—

23 months	20.65	74.65	74.2	+ 0.4
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Hence by distilling off a portion, the increase in the vapour pressure was diminished from 1.9 cm. to 0.4 cm. Eleven days later, the vapour pressure was again observed. It had nearly regained its value before distillation :—

23 $\frac{1}{4}$ months	22.20	81.07	79.60	+ 1.47
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A portion was distilled off again :—

23 $\frac{1}{4}$ months	22.20	79.60	79.60	0.00
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The vapour pressure of the residue had now become equal to that of the moist liquid at the same temperature. The following day, however, an increase of 0.5 cm. was again observed.

Larger effects were observed in the case of a third apparatus, made of capillary-free Jena glass. This rapid drying was ascribed to the use of this prepared glass.

TABLE XXXIII.

APPARATUS III. (Capillary-free glass.)

Duration of Drying at Room Temperature.	Temperature of Observation, °C.	Pressure of Dried Liquid (cm. Hg).	Pressure of Moist Liquid (cm. Hg).	Drying Effect (cm. Hg).
—	19.80	72.1	72.2	— 0.1
10 months	18.20	67.8	66.0	1.8
10 $\frac{1}{2}$,,	19.75	73.1	70.8	2.3
11 ,,	19.55	73.0	70.3	2.7
16 ,,	22.90	85.4	82.1	3.3

After $13\frac{1}{2}$ months experiments were carried out at higher temperatures, with the following results:—

$13\frac{1}{2}$ months	20·75	77·59	74·4	3·2
—	25·23	95·33	90·9	4·4
—	29·55	113·20	110·8	2·4

Again the increase in the vapour pressure passed through a maximum.

The influence of intensive drying on the colour of the liquid was also investigated. Two pieces of apparatus, each containing an observation tube of exactly 5 mm. diameter, were filled with nitrogen tetroxide, but one contained purest distilled phosphorus pentoxide also. After twenty-two months, equal quantities of nitrogen tetroxide were condensed in the observation tubes of each piece of apparatus, and the colour of the liquid columns was compared at the drying temperature. The dried liquid had become darker brownish-red than the moist liquid.

From this work, it was concluded by Smits and his co-workers that the drying process brings about a shift of the inner equilibrium in the direction $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$, i.e. in the direction of an endothermic reaction. The results, which at first appeared to conflict with those of Baker and Mrs. Baker, were reconciled with them by supposing that in the method of boiling-point determination employed by the latter experimenters, a certain amount of the liquid evaporated before the boiling-point was reached. It was pointed out that although the inner equilibrium $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is shifted to the right-hand side, i.e. the side of the more volatile pseudo-component, by intensive drying, which causes an increase in the vapour pressure, a rise in the boiling-point may nevertheless be observed, for, before the boiling-point is reached, the liquid is partly evaporated, and while the inner transformations have become exceedingly slow, or have stopped completely, this evaporation will cause a change in the composition of the liquid, so that the vapour pressure, which showed an increase at first, now will show a decrease, corresponding with a rise of boiling-point. If the boiling-point had been observed with the intensively dried liquid boiling under a reflux condenser, while the volume of the vapour was kept very small, a fall in the boiling-point should have been found, assuming the absence of superheating.

Similar results were obtained at about the same time by the author.¹ Nitrogen tetroxide was dried for six months by alternate distillation through phosphorus pentoxide. It was then

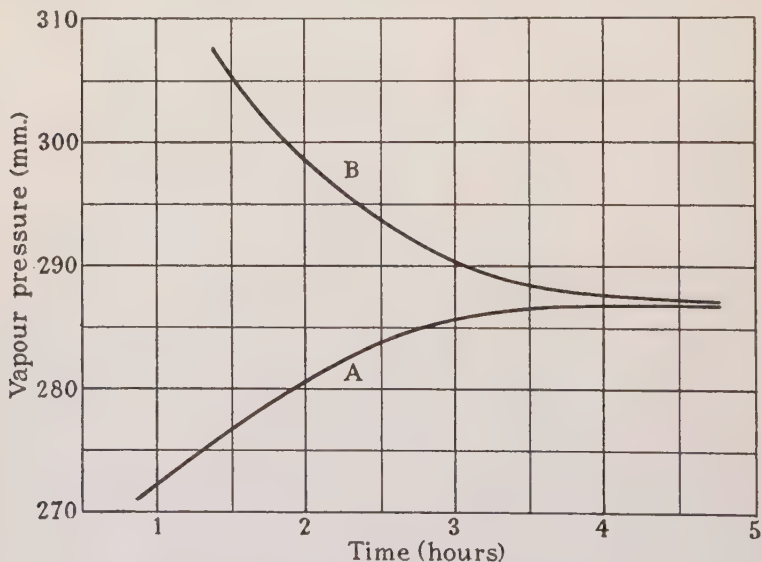
¹ *J. Chem. Soc.*, 1927, 867.

found that the vapour pressure was raised throughout the temperature range 0° to 30° C.; the results obtained are given in Table XXXIV.

TABLE XXXIV.

Temperature. °C.	Vapour Pressure (mm.).		
	Dry.	Wet.	Change.
0.0	282.6	264	19
5.2	370.3	348	22
15.2	595.8	571	25
15.9	615.4	591	24
19.6	727.8	704	24
20.5	757.9	736	22
24.2	890.5	869	21
24.7	910.3	890	20
29.0	1100.5	1080	20

It was also found that on change of temperature the vapour pressure first obtained was dependent on the previous history

FIG. 31.—Vapour Pressure—Time curves at 0° C.A after cooling to -10° .B after heating to 19.6° .

of the system. Thus after the tetroxide had been frozen out in solid carbon dioxide and alcohol, the initial vapour pressure at 0° C. was much lower than when the liquid had been cooled only

to -10°C . In each case the vapour pressure did not remain constant but rose slowly, being about six hours in attaining a constant value, this final value being equally approachable from either direction. Several vapour pressure-time curves were taken, two examples being shown in Fig. 31. These slow changes were attributed to the slow internal changes in the system consequent upon the temperature change.

CHAPTER XX.

HYDROCARBONS.

Hexane.—As has been indicated previously, hexane was one of the series of liquids dried by Baker.¹ Before distilling into the drying apparatus proper it was shaken for some days with phosphorus pentoxide, so as to give it a thorough preliminary drying. After standing for eight and a half years, the boiling-point was determined. A temperature of 82° was reached before any bubbles appeared in the liquid. The tube connecting the two flasks of the drying apparatus was then accidentally broken, and the liquid was left exposed to the atmosphere overnight. The following morning it was expected that the boiling-point would have fallen, but it was still 81° by the thermometer in the liquid. Hence it appears that once the boiling-point of hexane is raised by intensive drying, it only attains a normal value again comparatively slowly. Some of the liquid was transferred to a new distilling flask, which had not been specially dried. The temperature of ebullition as measured by the thermometer in the liquid was 81° , whilst that in the vapour was 68.4° , the original boiling-point.

Although the actual surface tensions of the moist and dry specimens of hexane were not quoted by Baker, he stated that they indicated that the factor by which the molecular weight should be multiplied was 3.16 for the dried compound, and 0.92 for the moist. He noted that Ramsay and Shields gave a value of 0.93 for normal octane, and, as there is no possibility of dissociation in the cases of these liquids, it was concluded that the liquids described by them as "normal" must have been to some extent dissociated, and the true value of k should be at least 2.28 instead of 2.121.

The change in the vapour pressure of hexane on intensive drying was investigated in some detail by Smits, de Liefde, Swart, and Claassen.² They used an apparatus of the form illustrated in

¹ *J. Chem. Soc.*, **121**, 568 (1922).

² *Ibid.*, 1926, 2657.

Fig. 25, constructed of capillary-free Jena glass. Vapour pressure determinations were made from time to time during the progress of the drying. The pressures read at the drying temperature are shown in the first five lines of Table XXXV. These show that the intensive drying in this case brings about a decrease in the vapour pressure at the drying temperature and were interpreted as indicating that the inner equilibrium is shifted in the direction of the less volatile pseudo-component.

After seven weeks, the vapour pressure was also taken at temperatures above the drying temperature. These results given in lines 6 to 8 of Table XXXV. show that the drying

TABLE XXXV.

	Duration of Drying at ca. 40° C.	Temperature of Observation, ° C.	Pressure of Dried Liquid (cm. Hg).	Pressure of Moist Liquid (cm. Hg).	Drying Effect (cm. Hg).
1	—	42·20	30·80	31·00	— 0·20
2	4 weeks	42·10	30·45	30·90	— 0·45
3	7 "	42·20	30·48	31·00	— 0·52
4	10 "	40·15	28·05	28·70	— 0·65
5	14 "	46·13	34·90	35·80	— 0·90
6	7 "	42·20	30·48	31·00	— 0·52
7	7 "	50·76	41·75	42·30	— 0·55
8	7 "	61·20	59·42	60·20	— 0·78
9	14 "	42·8	20·60	31·60	— 11·00

effect increased as the temperature was raised. The last line, a reading taken after a portion of the liquid had been distilled off, showed that such treatment causes a very large decrease in the vapour pressure. This low vapour pressure, however, was not constant, but rose slowly, so that after two and a half hours the decrease was again about a centimetre.

Although the apparatus was in a thermostat, it was considered to be possible that, the liquid being partially distilled off, the temperature might have decreased. The following experiment was therefore carried out. The apparatus was taken out of the thermostat and placed on the table; after two hours it had cooled to room temperature, the vapour pressure then being about 15 cm. It was then again placed in the thermostat, the rise of vapour pressure with time being noted. The vapour pressure rose very rapidly, and the curve obtained in this way showed a very great difference from that obtained after distillation. They considered that this proved that the slow rise of the vapour pressure

after distillation was due to a slow inner transformation, and concluded that the equilibrium was not yet quite fixed, but that the inner transformations were already very slow. It may be pointed out, however, that they should have observed some retardation in the attainment of a constant vapour pressure after cooling to room temperature for two hours. Although this period would probably have been insufficient for complete attainment of the abnormal (i.e. "dry") inner equilibrium corresponding to the lower temperature, nevertheless a change in this direction, i.e. towards the side of higher complexity, must have occurred to some extent; and, as has been shown by the present author in the case of nitrogen tetroxide, on warming again to the higher temperature, the vapour pressure only slowly attains a constant value. It is quite probable, however, that the inner equilibrium would be much less disturbed by the cooling than by the removal of a fraction.

The effect of fractionation was later studied in more detail.¹ *n*-Hexane was dried in a bath at 42.88° C. for twenty weeks in an apparatus of the form shown in Fig. 24. A similar apparatus from which the phosphorus pentoxide had been omitted was also included in the same thermostat. Whilst the apparatus was still in the thermostat, the right-hand side of the mercury gauge was connected with a condensation tube, a closed mercury manometer, and an air pump. Whilst the condensation tube was cooled with liquid air the pressure was so much diminished that on opening the tap the hexane bubbled through the mercury of the gauge and condensed in the condensation tube. When a sufficient amount had distilled off, the pressure on the right-hand side of the gauge was so far increased that the mercury surface stood at the same height in both limbs of the indicator. The pressure measured in the closed mercury manometer was also equal to the vapour pressure of the hexane. In the case of the moist specimen half the hexane was rapidly distilled off and then the vapour pressure measured after various periods of time. Only during the first two minutes was a very small diminution of the vapour pressure to be observed, and this can naturally be ascribed to the lowering of the temperature through the rapid evaporation of the liquid. However, the hexane which had been intensively dried for twenty weeks behaved very differently. Here distillation was visibly slower and a smaller part, only a quarter, of the liquid was distilled off. In spite of this, however, the vapour pressure was diminished by

¹ *Z. physikal. Chem.*, **129**, 33 (1927); *Chem. Weekblad*, **25**, 82 (1928).

11 cm. This vapour pressure, however, was not constant, but increased with gradually diminishing velocity, so that after three and a half hours the initial vapour pressure was again attained. This again showed that the inner equilibrium was not yet quite fixed, but that it was so far inhibited that on distillation the liquid behaved as a mixture. It is of interest to note here also that when the contents of this apparatus were later exposed for a short time to an evacuated but not intensively dried space, the hexane afterwards behaved again completely as though it were in the moist condition. The change in vapour pressure also completely disappeared, this giving still further support to the conclusion that this effect is only to be ascribed to the intense degree of dryness obtained by this process.

In order to be able to determine the vapour pressure of the distillate as well as that of the residue, an apparatus was employed of the type shown in Fig. 26. As this apparatus contained a large amount of mercury in the manometer *C* the period of drying required was somewhat greater than in the cases previously described. After six months' drying, during a few weeks of which the apparatus was kept at 60° C. in order to accelerate the drying process, the bulb *B* was placed in a bath at 0° C., whilst the remainder of the apparatus was at room temperature. As soon as all the hexane was condensed in *B*, the bulb round *B* was removed and placed round *B'*. The hexane distilled slowly from *B* to *B'*, and when half had distilled over, *B* was also immersed in an ice bath. Dry air was admitted by taps *M*₂ and *M*₁ till it drove the mercury in *D* into the limbs of the manometer *C*. At this moment the mercury was lower on the *B* side than on the *B'* side, since the temperature of *B* was still somewhat higher than that of *B'*; it is important to notice that this situation was afterwards reversed.

The whole apparatus was immediately placed in a large thermostat at 18.4° C., a little below room temperature. The first reading was taken two minutes after the immersion in the thermostat, this being the time found by a control experiment with moist hexane to be sufficient for attainment of thermal equilibrium. The difference between the vapour pressure of the distillate and that of the residue was initially 4 cm., but this decreased with time and after half an hour practically disappeared.

The effect observed was supposed to be partially a result of the distillation carried out at 0° C., and partly due to the rapid distillation the liquid undergoes on the rapid transference from the bath at 0° C. to one at 18.4° C. The double apparatus used was so constructed that the volume on the side of the vessel *B*

with the residue was greater than that of the side containing B' for the distillate, so that the residue was more strongly vaporised than the distillate when the apparatus was plunged into the bath at 18.4°C . The results obtained here again show that the inner transformations were not yet fixed, for the inner equilibrium set in again after a lapse of time. The fact that the vapour pressures of the distillate and residue gradually became equal was also regarded as additional evidence that the hexane did not react with the phosphorus pentoxide, but still remained in the pure state.

It was found to be preferable to carry out these measurements in a bath at below room temperature, owing to the poor thermal conductivity of phosphorus pentoxide, which requires a long time to acquire the temperature of a thermostat, especially if liquid is being evaporated from its surface. It was found later that the only method whereby no complications can enter is that employing the principle of Watt, in which case after fractional distillation the apparatus is not transferred to a constant temperature bath, but is left at room temperature, whilst only the vessels B and B' are placed in baths at 0°C . or at any other temperature just below that of the room.

Benzene.—The benzene which was used in Baker's historic series of experiments ¹ was first dried over phosphorus pentoxide and then distilled into the drying apparatus proper. The latter was provided with two thermometers, one to record the temperature in the liquid and the other that in the vapour. The temperature of the oil bath was raised very slowly during the boiling-point determinations. When it had reached 105°C . there was manifest evaporation, and liquid dropped from the upper thermometer, which gave a constant reading of 80°C . On one occasion these drops, falling on the surface of the hot liquid below, formed a globule, 12 mm. in diameter and 5 mm. deep, which persisted for more than a minute. When it coalesced with the rest of the liquid, it did so without any disturbance, and there was no perceptible increase in pressure in the apparatus. The liquid boiled quite steadily at 106°C . Some of the liquid was distilled from the apparatus into a distilling flask and left for a day exposed to moist air. Its boiling-point was now 105°C . It was then shaken with water, and it was found that water could be boiled through the layer of benzene, only slow evaporation of the latter taking place. In time, however, the liquid regained its normal boiling-point. The original apparatus was allowed to cool and

¹ *J. Chem. Soc.*, **121**, 568 (1922).

draw in air dried by sulphuric acid and phosphorus pentoxide, but a month later its boiling-point was 81°C . The boiling-point was found to be 106° in three different pieces of apparatus which had been sealed up within a few days of one another in March, 1913. In two others, dried for about two months longer, the boiling-points were each 118°C . The ebullition in the two latter tubes was not so steady as in the former, being more violent and suggesting some degree of ordinary superheating.

Surface tension measurements showed that after drying for a year, benzene gave in a tube of 0.111 mm. radius a capillary rise 13.73 mm. higher than in the undried liquid at 16.5°C ., and 15.65 mm. higher at 35°C . (Baker does not quote the actual rises measured.) The multiples of the molecular weight calculated from this data according to the method of Ramsay and Shields are 3.39 for the dry liquid and 1.28 when undried.

Later,¹ at the suggestion of Smits, Baker carried out a partial fractionation of the dried benzene. The neck of a flask of dried benzene was closed by a paraffined cork, through which a thermometer passed. There were about 15 c.c. of the dried liquid in the flask. The tip of the delivery tube was broken under dried mercury, and the temperature of the oil bath raised slowly to 105°C . without apparent ebullition. The temperature by the thermometer in the vapour was 81° when evaporation through the mercury was readily apparent, but rose to 87° as evaporation proceeded. This seemed to indicate a true fractionation, the non-associated liquid coming off first.

Baker also found that the melting-point of the benzene which had been dried for ten years was 6.0°C ., whilst a similar specimen dried for only a month melted at 5.4°C .

In view of the remarkable effects obtained with this liquid by Baker, benzene was chosen by Smits as the first liquid upon which to test his theory of intensive drying and its bearing on his theory of allotropy.² The apparatus he employed is illustrated in Fig. 32. All tubes except *E* were sealed off, and the apparatus tested to see if the whole was gas-tight by connecting *E* to a mercury diffusion pump. *G* was then sealed to the phosphorus pentoxide distilling tube *XY*. The dimensions of the latter were 75 cm. by 2.5 cm. The wider part was 3.5 cm. diameter. In the narrowest portion a glass stopper provided with points was placed, so that, while free channels were left round it, there was no danger of impure phosphorus pentoxide passing into *B* during the filling of the bulb. The distillation tube was all heated to

¹ *J. Chem. Soc.*, **123**, 1223 (1923).

² *Ibid.*, **125**, 1069 (1924).

redness and filled with phosphorus pentoxide by the plunger and piston device. During filling, carefully dried oxygen was passed through the apparatus in the reverse direction, right to left. The distilling tube was then connected with the oxygen drying apparatus by means of a rubber stopper, and while the oxygen was sent through at about 2 to 3 bubbles per second, the tube was heated to 220°C . During the sublimation into *Y*, the dis-

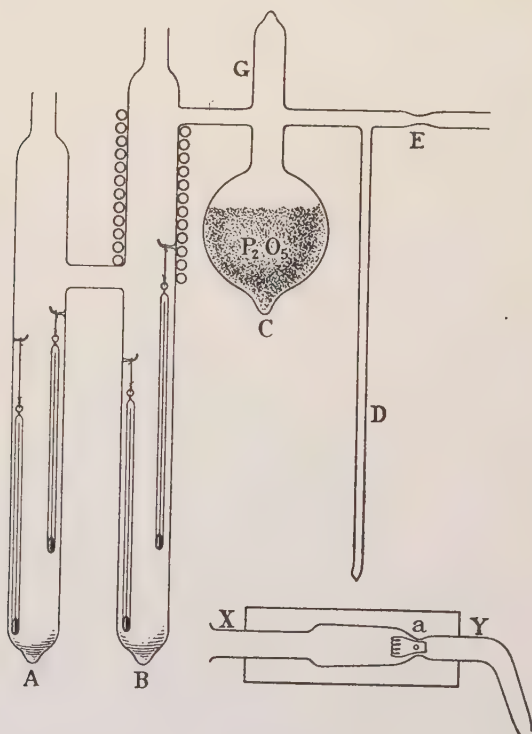


FIG. 32.

tilling apparatus was heated to redness and oxygen forced to go through the heated bulb or tube to remove moisture. The open tube was connected with a phosphorus pentoxide drying tube and a sulphuric acid wash-bottle, in order to prevent moist air from creeping back into the apparatus. The pure phosphorus pentoxide which deposited in *Y* was then introduced into the bulb *C* by tapping *Y* or by subliming it further. Tube *E* was sealed off, and *D* opened under previously boiled mercury. Pure dried benzene was introduced into *B*, the latter cooled in solid carbon

dioxide and alcohol, the upper end sealed off, and after the oxygen current was stopped, also the vertical tube of the bulb *C*. A water-cooling spiral was wound round *B*, and by adjustment it was possible to distil the benzene from *B* into *A* without allowing it to pass into *C* and without its running down the thermometer hanging in the vapour. Since *D* was opened under mercury, the boiling-point could be determined at one atmosphere pressure. The results so obtained are given in Table XXXVI.

TABLE XXXVI.

Date.	Liquid Temperature (° C.).	Vapour Temperature (° C.).
June 2nd . . .	80	80
Aug. 15th . . .	81.5	81
Feb. 23rd . . .	87	85

At this stage a crack developed in the apparatus, and although this was sealed immediately, the abnormality had almost completely disappeared a month later, as the following results show :—

March 23rd . . .	81.5	80.9
June 29th . . .	83	81
Feb. 7th . . .	86.6-89	84.8-87.7

Benzene was also one of the liquids investigated by Mali,¹ whose results are given in Table XXXVII. It is noticeable that the lowering of the vapour pressure was greater with the benzene dried at the higher temperatures than at the lower. This was found to be true also for the other liquids he employed.

TABLE XXXVII.

Dried at 27° C.		Dried at 43° C.	
Temperature, ° C.	V.P., cm.	Temperature, ° C.	V.P., cm.
23.7	8.55	22.3	8.05
31.0	12.0	31.2	11.85
35.4	15.05	36.0	14.60
40.1	17.35	41.5	18.25
46.0	21.8	48.1	21.25
50.6	25.75	—	—
57.0	32.55	—	—
60.1	37.1	—	—
63.7	42.75	—	—

Mali also found that the refractive index of the benzene changed after the intensive drying, the deviation obtained with a certain prism being 66° 58' with ordinary benzene, and 66° 44' with the dried material. Hence he concluded that from the Gladstone and Dale equation $(\mu - 1)/d = \text{constant}$ that the density of dry benzene is greater than that of the undried material.

¹ *Z. anorgan. Chem.*, **149**, 150 (1925).

According to Baly,¹ the refractivity of benzene is greatly decreased on careful drying, a phenomenon which he considered could be explained by the disappearance of the absorption band in the near ultra-violet. The rise in boiling-point observed on complete drying he calculated to be equivalent to the loss of one quantum per molecule at the characteristic of benzene in the infra-red.

The change in the latent heat of evaporation of benzene on intensive drying was determined by Baker.² A modification of Berthelot's method was employed, using an apparatus of the form shown in Fig. 33. Benzene, carefully purified and distilled from phosphorus pentoxide, was contained, together with phosphorus pentoxide, in the upper bulb. After standing for three and a half years it was distilled by means of a ring burner into a graduated lower tube, immersed in a known weight of water contained in a Dewar vessel. The boiling-point of the liquid was then determined. From the volume of liquid distilled and the rise in temperature of the water, the latent heat of evaporation could be calculated. With two different pieces of apparatus, the latent heats for 1 gram of the dry benzene were 57.2 and 58 respectively, instead of 83, the normal value. The boiling-point of the dry benzene was 94°, so in order to bring this result in conformity with Trouton's Rule, the molecular weight of benzene must be 136 instead of 78. The objections raised by Smits against this deduction have already been discussed (p. 170).

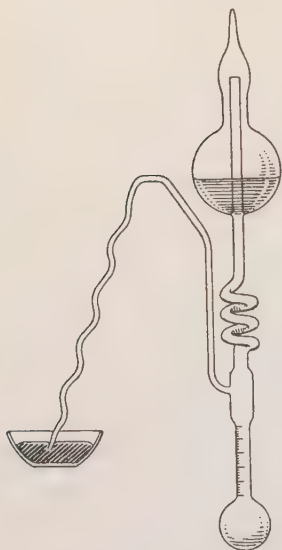


FIG. 33.

Toluene.—The only series of experiments on intensively dried toluene that have yet been published are those of Mali.³ Unfortunately, however, in this case the apparatus broke after one reading, and so the vapour pressures at higher temperatures could not be determined. At 27.0° C., the toluene which had been dried at 27° C. gave a vapour pressure of 2.7 cm., whilst that dried at 42° C. gave a pressure of 2.2 cm. Hence it appears that the vapour pressure of toluene decreases with intensive drying.

¹ *Trans. Faraday Soc.*, **21**, 582 (1926). ² *J. Chem. Soc.*, 1928, 1051.

³ *Z. anorgan. Chem.*, **149**, 150 (1925).

CHAPTER XXI.

OTHER LIQUIDS.

Carbon Tetrachloride.—The carbon tetrachloride used in Baker's experiments ¹ was purified by saturating it with chlorine, boiling to drive off the gas, and then allowing to stand in contact with solid caustic soda. It was distilled into a bottle containing phosphorus pentoxide, and redistilled into the drying apparatus proper a month later. It was tested early in 1914, but the record of the temperature of sealing was lost. Hence it was not known when it was safe to break the tip of the long tube under mercury. This was carried out prematurely, when the temperature was 100° C., and the mercury rose 80 mm. in the long tube, so under the diminished pressure of 670 mm. the carbon tetrachloride did not boil. At 112° C. ebullition commenced.

Using the same method as that employed in the cases of the other liquids, Mali obtained the vapour pressures given in Table XXXVIII.² Once again it will be observed that the lowering of

TABLE XXXVIII.

Dried at 27° C.		Dried at 43° C.	
Temperature (° C.).	V.P. (cm.).	Temperature (° C.).	V.P. (cm.).
23·8	10·35	23·9	10·1
30·8	14·2	30·6	13·7
37·3	18·15	37·1	17·7
40·1	21·25	41·3	19·95
50·6	31·15	51·3	27·15
60·5	44·15	55·8	32·25
—	—	61·3	39·6
—	—	64·9	45·95

the vapour pressure was greater at the higher temperature than at the lower.

Carbon Disulphide.—In this case, Baker employed a specimen of liquid which had been purified by J. W. Rodger in 1894. The bottle in which it had been stored contained phosphorus pentoxide and the stopper was covered by oil silk. The carbon disulphide

¹ *J. Chem. Soc.*, **121**, 568 (1922).

² *Z. anorgan. Chem.*, **149**, 150 (1925).

was distilled into a tube in which it was dried by phosphorus pentoxide, the boiling-point being then 49.5°C . The tube was left sealed up for a year. On testing at the very low barometric height of 730 mm., the first sign of vaporisation was found to occur at 60°C . The vapour was seen to condense on the tube, and the liquid ran down in oily drops which coalesced with the main body of the liquid without any sudden production of vapour. The first bubble was seen at 80°C ., and at 81° ebullition was general throughout the liquid.

Carbon disulphide was also one of the liquids dried by Mali, who obtained the results shown in Table XXXIX.

TABLE XXXIX.

Dried at 27°C .		Dried at 43°C .	
Temperature ($^{\circ}\text{C}$.),	V.P. (cm.),	Temperature ($^{\circ}\text{C}$.),	V.P. (cm.),
21.8	31.08	24.0	33.53
26.0	36.63	30.4	42.23
30.9	44.38	35.0	49.73
35.8	53.28	40.2	60.03
40.3	61.63	45.1	70.38
45.0	72.58	—	—
46.4	76.08	—	—

That the vapour pressure of carbon disulphide is lowered by intensive drying was also confirmed by Smits,¹ who found that after drying for twenty-six months at 20° to 23°C . the vapour pressure of carbon disulphide at 20.55°C . was changed from 30.86 cm. to 29.56 cm., a lowering of 1.30 cm.

Ethyl Ether.—Ether was another of the liquids investigated by Baker, but in this case it was not left in contact with phosphorus pentoxide, and drying was dependent on the removal of moisture from the vapour phase. The liquid tended to collect in the part of the apparatus containing the drying agent, but was distilled off without opening the apparatus. Boiling began at 83°C . Some of the liquid was distilled into another flask, dried only by heating and drawing air through it. This boiled at 47° , the thermometer in the vapour reading 35°C . The next day the liquid, exposed to comparatively moist air, boiled at 36°C . In this case the rate of recovery of the normal state was much more rapid than in the cases of benzene and of hexane.

The vapour pressure of the ether was determined, using a dried barometer tube of mercury, surrounded by a water jacket. At 20°C . it gave a vapour pressure of 374 mm., as against a normal value of 442 mm. (Ramsay and Young).

The vapour density of the ether was also measured.² The

¹ *Z. physikal. Chem.*, **129**, 33 (1927).

² *J. Chem. Soc.*, **123**, 1223 (1923).

value obtained was 81.7 as against a normal density of 37. However, both these vapour pressure and vapour density measurements have been severely criticised by Smits, as has been indicated in an earlier chapter.

Mercury.—As early as 1900,¹ Baker carried out vapour density determinations on very carefully dried mercury, in order to find out if the vapour, which is under ordinary circumstances monatomic, becomes more complex under these conditions. These experiments were carried out at the boiling-point of sulphur; the densities obtained were 107.6, 104.4, 112.5, and 108.1, so he concluded that the vapour was monatomic even when dry.

Later² mercury was one of the liquids chosen by Baker to test the effect of intensive drying on boiling-point. The mercury employed had been purified by shaking with mercurous nitrate, distilling *in vacuo*, shaking in air, and then redistilling. After drying for nine years over phosphorus pentoxide, the boiling-point was determined by heating in a short wide silica tube closed at the bottom and converted into an electric furnace by a coil of nickel-chromium wire, covered by a layer of asbestos cloth. The temperature was determined by the simultaneous use of a platinum-rhodium couple and by a Jena glass nitrogen filled thermometer. It was maintained at 360° for half an hour. Not only was there no boiling, but only the faintest trace of sublimate appeared above the surface of the liquid. Bubbles of vapour first escaped at 420°, but active ebullition was only apparent at 425°.

These observations were followed up by Smits,³ who employed an apparatus of the type shown in Fig. 34 wherein the mercury

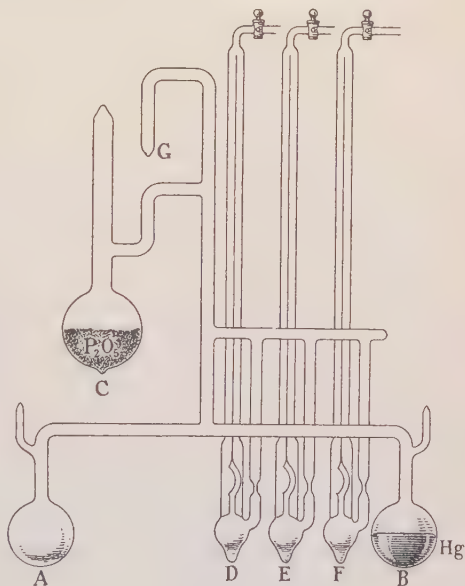


FIG. 34.

¹ *J. Chem. Soc.*, **77**, 646 (1900).

² *Ibid.*, **121**, 568 (1922).

³ *Chem. Weekblad*, **25**, 82 (1928).

could be distilled between bulbs *A* and *B*, in a highly evacuated space which was dried by phosphorus pentoxide. The apparatus possessed three glass spring indicators into which the dried mercury could be transferred. After nearly two years' drying, one of the tensimeter bulbs was filled with mercury, sealed off, and the vapour pressure of the mercury measured at different temperatures, but no difference from undried mercury was detected. After $3\frac{3}{4}$ years' drying, the second tensimeter was filled with mercury and sealed off. This specimen gave the results shown in Table XL.

TABLE XL.

Temperature.	Vapour Pressure of Mercury in cm. Hg.		
	Dried for $3\frac{3}{4}$ Years.	Moist.	Decrease, cm. of Hg.
170	0.15	0.61	0.46
194	0.8	1.41	0.61
206	1.35	2.09	0.74
230	2.8	4.28	1.48
248	5.35	7.03	1.78
273	11.4	13.23	1.83
291	18.05	20.13	2.08
297.5	22.45	23.26	0.81
309.5	30.1	30.1	0.0
332	47.7	47.7	0.0
347.5	64.0	64.0	0.0

When plotted graphically, these results give the curves shown in Fig. 35. At 300° the vapour pressures of intensively dried and moist mercury are the same. Hence it appears that the degree of drying which affects the vapour pressure at lower temperatures is insufficient to do so at this temperature. This result is exactly analogous to that obtained with ammonium chloride (see p. 66). After heating to 350° and then cooling, the same vapour pressure curve was traced. On filling the third gauge, a crack developed, so no further investigation could be carried out.

Nitrobenzene.—It was found by Roberts and Bury¹ that on several occasions when nitrobenzene was kept over phosphorus pentoxide in a distillation apparatus for over a week, its behaviour on distillation recalled Baker's observations. The flask containing nitrobenzene stood in a boiling saturated solution of sodium chloride, nevertheless it could only be made to boil with difficulty by reducing the pressure to a minimum. The bath could sometimes be evaporated to dryness without distillation beginning; once boiling started, however, it proceeded regularly and quietly, and a thermometer suspended in the vapour registered a temperature of about 90°C . When nitrobenzene was distilled im-

¹ *J. Chem. Soc.*, **123**, 2037 (1923).

mediately, without long drying, boiling started without difficulty as soon as the bath became hot, the temperature registered being the same as before.

Nitromethane.—According to Williams¹ the form of the specific heat-temperature curve of nitromethane is strongly dependent on the extent to which the material has been dried.

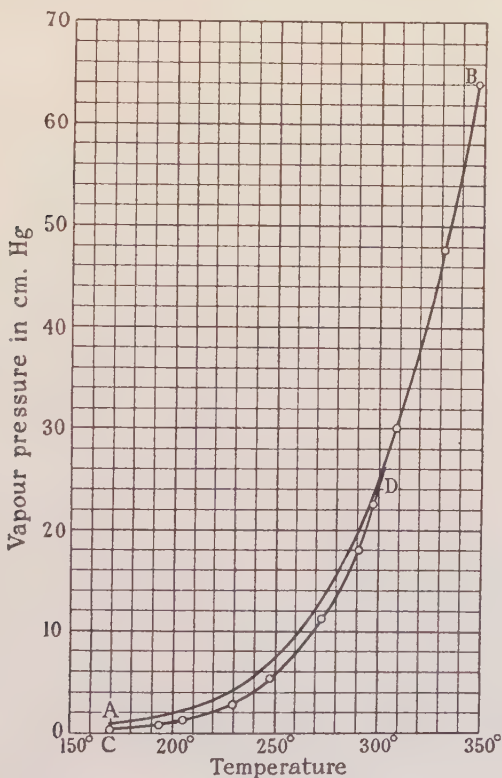


FIG. 35.

The empirical equations giving the specific heat at constant pressure (C_p) as a function of the temperature ($t^\circ \text{C.}$) are :—

- (a) For nitromethane dried by means of phosphorus pentoxide,
 $C_p (30^\circ \text{ to } 70^\circ \text{ C.}) = 0.397_6 - 0.00033_8 t + 0.0000081_5 t^2.$
- (b) For nitromethane dried by means of calcium chloride,
 $C_p (15^\circ \text{ to } 70^\circ \text{ C.}) = 0.420_9 - 0.00076_1 t + 0.0000060_5 t^2.$

¹ *J. Amer. Chem. Soc.*, **47**, 2644 (1925).

On the other hand, there was no sign of any irregularity in the temperature coefficient of the density or of vapour pressure corresponding to the irregularities in the temperature coefficients of the specific heat. The absorption spectrum of nitromethane was the same whether examined as received, after drying over calcium chloride, or after drying over phosphorus pentoxide. The effect of moisture on some of the physical properties is shown in Table XLI.

TABLE XLI.

Property.	Nitromethane with 0.20 per cent. H_2O .	From Manufacturer.	Dried with $CaCl_2$.	Dried with P_2O_5 .
C_p (15° to 19° C.)	0.4145	0.4100	0.4065	0.4010
n_D^{22}	1.38095	1.38076	1.38065	1.38052
d_4^{25}	1.1312 ^a	—	1.1320	1.1322

N.B.— $a = 0.10$ per cent. water.

Several preliminary experiments on the intensive drying of nitromethane showed slight rises in the boiling-point (0.5° over a period of six months).

CHAPTER XXII.

SOLIDS.

Sulphur Trioxide.—Sulphur trioxide has long been known to be capable of showing remarkable complexity, its properties differing strangely according to the exact method used in its preparation. In fact it was described as a “chemical chameleon.” Hence it was supposed by Smits and Schoenmaker¹ that on

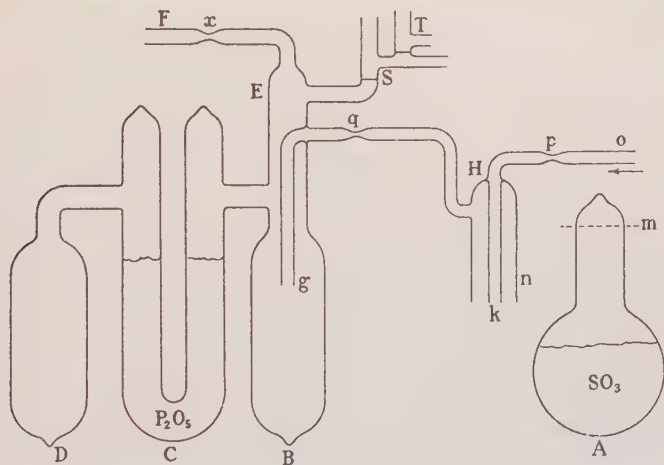


FIG. 36.

drying over phosphorus pentoxide it would be so dry that the velocity of inner transformation would be so slow that the single substance would behave as a mixture, the ingredients of which could be separated and their properties severally examined.

For this purpose they used a Jena glass apparatus of the type shown in Fig. 36. Two tubes, *B* and *D*, were sealed to a *U*-tube *C*. Tube *B* contained an inner tube, *g*, which led to a tube *Hn* surrounding a tube *ko*. The upper part of tube *B* ended on one

¹ *J. Chem. Soc.*, **125**, 2554 (1924) ; 1926, 1108.

side in a tube *F*, leading to a mercury diffusion pump, and on the other side in a *T*-piece with septum *S*.

Whilst air, dried consecutively by strong sulphuric acid and phosphorus pentoxide, was passed through the tube *ok*, the neck of a cooled bulb, *A*, containing pure sulphur trioxide, was cut off at *m*, and immediately sealed to the tube *Hn*. The *U*-tube *C* was now filled with phosphorus pentoxide, and the ends were sealed off whilst dry air was circulating through the apparatus. The tube *ok* was sealed at *p*. A *U*-tube between *F* and the pump

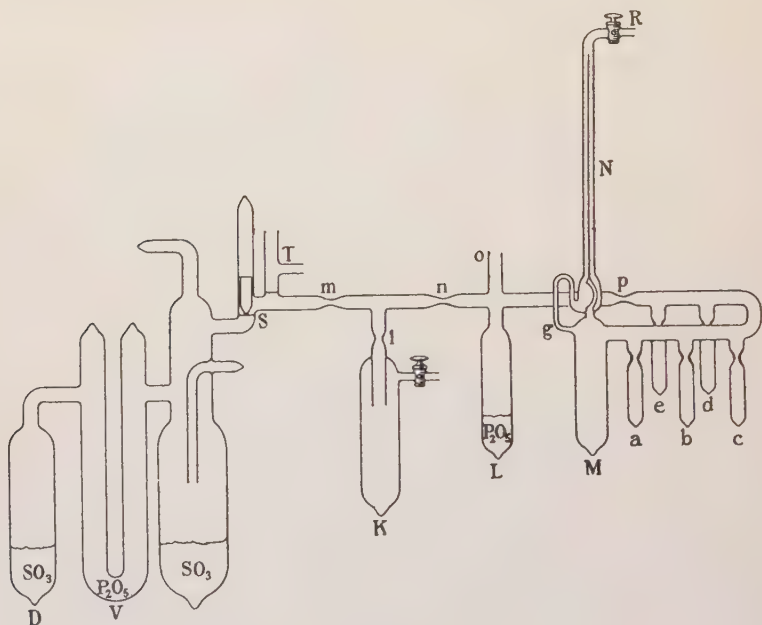


FIG. 37.

was cooled in liquid air, the bulb *A* cooled in alcohol and solid carbon dioxide, and the apparatus evacuated and sealed off at *x*. The sulphur trioxide was distilled from *A* into *B* and *q* was sealed off. It was then distilled from *B* to *D*, and from *D* to *B*, one vessel being cooled in carbon dioxide and alcohol whilst the other remained at room temperature. This drying process was repeated every day for a month or longer.

Their vapour pressure apparatus is shown in the right-hand half of Fig. 37. *MN* is a glass spring indicator. The bulb *M* was connected to a wide horizontal *U*-tube to which five vertical

small tubes with capillaries, *a*, *b*, *c*, *d*, and *e* were sealed. The remainder of the connections are obvious from Fig. 37.

Tube *O* was sealed to an apparatus so that pure phosphorus pentoxide could be distilled in a current of intensively dried air. Previous to this, the apparatus had been heated in a current of dry air, driven through every tube and vessel. The capillary ends of these tubes and vessels were then sealed off successively. After distilling the phosphorus pentoxide into *L*, tube *O* was sealed off, and tube *R* connected to the mercury pump. After the apparatus had been heated with a large Teclu burner and evacuated until a high vacuum was reached (10^{-6} mm.) connection between the mantle of the glass spring and the vessel *M* was broken by sealing off the capillary tube *g*.

Bulb *D*, containing the sulphur trioxide was now cooled in a mixture of alcohol and solid carbon dioxide, and septum *S* broken by shaking. The delivery tube of *K* was connected to the vacuum pump, and while this vessel was cooled in liquid air, a portion of the sulphur trioxide was distilled into *K*, *D* being allowed to warm up to room temperature (18° C.). By this means a solid distillate was obtained in *K* with an initial melting-point of 80° C. After resolidification, the melting-point was 32° C. *D* was then cooled again to -80° C., and the capillary *l* sealed off. Some sulphur trioxide was now distilled into *L*, and the capillary at *n* sealed off.

The apparatus was now set up rigidly, *L* cooled in liquid air, and *R* connected to a high vacuum pump in order to fix the zero position of the needle of the glass spring by means of two strips of paper on which were drawn very fine lines. The whole apparatus was placed in a thermostat, and tube *R* connected to a mercury manometer. As required, the pressure was changed until the needle of the glass spring gauge was in the zero position.

The sample of sulphur trioxide obtained in this way was an ice form, and above 18° C. was a clear liquid without a trace of solid. By cooling in liquid air, or on distilling repeatedly from 18° to -80° C., the asbestos form could always be obtained, but so long as the other, more volatile, form was present, the pressure was that of the latter.

The first determinations of the vapour pressure of the dried material are shown in Curve I. (Fig. 38). Melting occurred over a temperature range, and during the melting process the pressure sank. After the apparatus had stood for eighteen hours at 18° C., the measurements were repeated, with the results shown in Curve II., whilst after a further eighteen hours, still at 18° C., the values obtained were as shown in Curve III. The

result was that for every new series of determinations a lower curve was obtained for the equilibrium solid-vapour, the same curve for the equilibrium solid-liquid-vapour, and a slightly lower curve for the equilibrium liquid-vapour

Having condensed the sulphur trioxide in *M*, a portion was distilled into tube *e*. After sealing off tube *e*, the vapour pressure was redetermined, with the results shown in Curve IV. This was

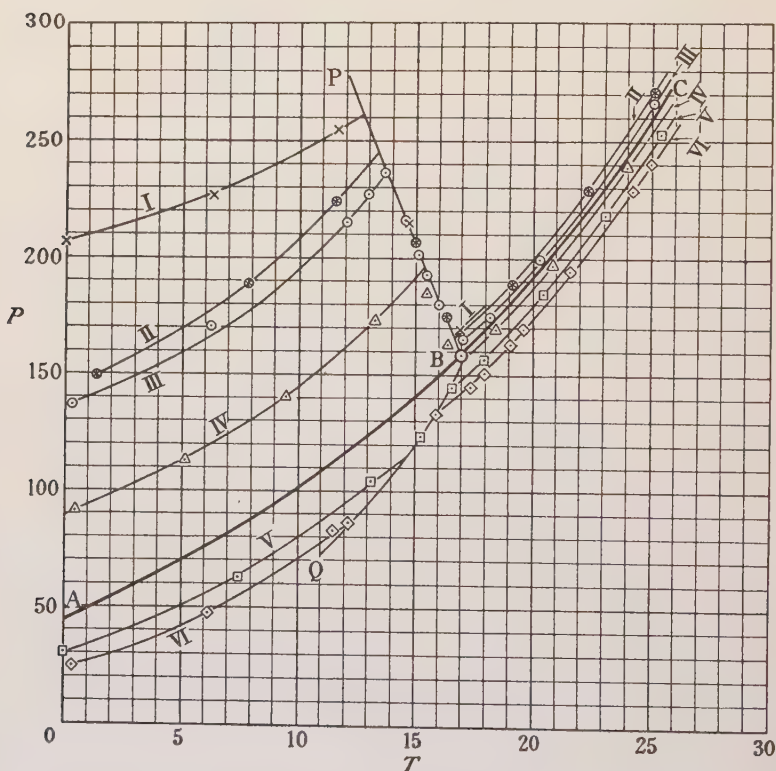


FIG. 38.

repeated with bulbs *d* and *c*, giving the curves shown V. and VI. The vapour pressure line of the solid phase, previously above that of the liquid, then lay below it, giving a part of a three-phase line S—L—G in which the pressure increased with rise of temperatures.

These results were considered to show that the ice-like form of sulphur trioxide when pure and dry behaves, not as a simple compound, but as a mixture, and that on removing a fraction of

the solid by distillation, the more volatile component distilled off first, leaving a residue with a lower vapour pressure. Similarly, the vapour pressure of a distillate, as exemplified by the sulphur trioxide when first introduced into *L* was at first abnormally high, but the inner state of the compound gradually changed towards the equilibrium condition, causing a gradual fall in the vapour pressure, corresponding with the gradual passage of the more volatile type of molecule into the less volatile.

In all, three distinct types of sulphur trioxide have been isolated, the ice-like form, a low melting-point asbestos-like form, and a high melting-point asbestos-like form, and the properties of each have been investigated. The last shows in a very re-

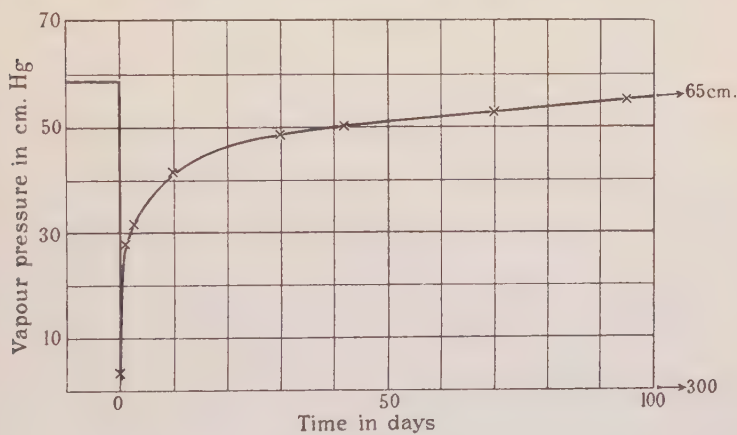


FIG. 39.

markable degree indeed the diminution in vapour pressure on distillation, a decrease from 59.1 to 3.7 cm. at 50° C. being observed in one case. The abnormally low vapour pressures were found to remain constant at room temperature, but at higher temperatures the vapour pressure increased with a velocity which decreased with time. Thus in the case cited above, the vapour pressure rose slowly as shown in Fig. 39, till after about 200 days it reached a value of 60 cm., and appeared to be approaching an asymptotic value of 65 cm., which was supposed to be the vapour pressure at this temperature with the pseudo-components in inner equilibria. Thus in this case the velocity of establishment of the inner equilibrium is imperceptibly slow at 18° C. ; at higher temperatures, however, this velocity increased. The observed phenomena were interpreted as indicating that this form is a

mixed crystal of at least two pseudo-components, differing widely in volatility and melting-point.

Attempts have also been made to investigate the different forms by the aid of X -rays,¹ but this does not seem to be possible, since all the spectragrams obtained were identical. Insolation with X -rays appears to enable the inner equilibrium to be attained quite rapidly, even in the absence of water. Thus a sample was taken of the high melting asbestos-like form in an apparatus consisting of a thin-walled glass capillary tube connected to a glass spring gauge. This was submitted to the action of Copper K_α rays, with the result that the vapour pressure gradually changed, as shown in Table XLII.

TABLE XLII.

Temperature (° C.).	Time (hours).	V.P. (cm. Hg).
18.0	0	10.8
18.0	1	22.2
18.0	4	43.1
18.0	8	46.1
19.7	10	46.3
19.7	13	46.3

Since the vapour pressure of the high melting, asbestos-like form in inner equilibrium at 19.7° C. is 46.4 mm., it is evident that the action of X -rays had caused rapid attainment of the inner equilibrium.

Phosphorus Pentoxide.—Since phosphorus pentoxide is capable of acting as a very powerful desiccating agent indeed, it might be anticipated that it would exert a great self-drying power, and that distillation of this compound would yield a more intensively dried compound than any other known. Such a dried compound would be expected to give very interesting results indeed.

With these considerations in view, preparations of very pure phosphorus pentoxide were made by Smits and Rutgers,² and their vapour pressures determined. The apparatus used had the form shown in Fig. 40. A bulb A , ending in a glass spring indicator, S , and a needle pointer P was sealed to a mantle B drawn out into a tube D which carried a stopcock K . The bulb A and the mantle B were connected by a capillary tube, C . After the apparatus made of high melting-point Jena glass or quartz had been steamed and dried, tube F was sealed to a phosphorus pentoxide distilling tube, whilst D was connected by a

¹ Smits, *Chem. Weekblad*, **25**, 89 (1928).

² *J. Chem. Soc.*, **125**, 2573 (1924).

short rubber tube with a *U*-tube filled with phosphorus pentoxide and then with a wash-bottle containing strong sulphuric acid.

The apparatus was heated to redness whilst carefully dried air was passing through the distilling tube. On distilling the phosphorus pentoxide, the sublimed oxide was deposited in the end of the distilling tube, from which it was distilled into *A* by further heating. The phosphorus pentoxide so obtained was an exceedingly fine crystalline substance. The capillary at *F* was then sealed off, and the apparatus evacuated by a mercury diffusion pump. When a vacuum of about 10^{-5} mm. was reached the capillary *C* was sealed, thus cutting off the tube *A* from the mantle tube *B*. The vapour pressure of the specimen at various temperatures was then determined.

The vapour pressure of the fine crystalline sublimate could only be determined up to 400°C. , since at higher temperatures it was transformed into a modification having a very low vapour

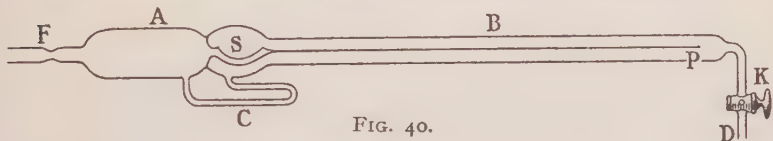


FIG. 40.

pressure. The vapour pressures of the different preparations varied with the velocity of distillation, an observation which was considered to prove that such preparations were not in a state of equilibrium. Provided that they were not heated to too high a temperature, they gave the same vapour pressures with rising or with falling temperature. Table XLIII. shows that at about 370°C. the vapour pressures of two preparations were 1.8 and 2.05 atmospheres respectively.

TABLE XLIII.

Preparation.	t° .	T° abs.	ϕ Pressure in cm. Hg.	P Pressure in Atmosphere.	T in P or $2.3025 T \log_{10} P$.
1	296	569	10.9	0.143	— 1105
	324	597	30.4	0.400	— 546.8
	351	624	67.5	0.884	— 76.7
	375	648	141.4	1.865	404
	406	679	323.7	4.259	984
2	276	549	7.2	0.095	— 1293
	304	577	22.0	0.289	— 716.6
	315	588	29.7	0.391	— 552.2
	361	634	122.1	1.608	300.9
	377	650	200.0	2.631	629

At about 400° C. the metastable volatile forms were transformed into a less metastable modification, and the vapour pressure fell continuously to 0.02 cm. An unlimited number of vapour pressure curves similar to the above could be realised, and, just as the initial preparations showed differences, so did the transformed modifications, although there the differences were not so large and it appeared probable that after sufficient time constant end values might have been obtained.

Another interesting fact was that the pure phosphorus pentoxide in the transformed modifications of low vapour pressure melted over a temperature range and not at one temperature. These results are given in Table XLIV.

TABLE XLIV.

t° C.	T° abs.	p Pressure in cm. Hg.	P Pressure in Atmospheres.	$T \ln P$ or $2.3025 T \log_{10} P$.
496	769	6.7	0.088	— 1867
517	790	12.4	0.163	— 1448
546	819	28.3	0.372	— 809.1
556	829	37.1	0.488	— 604.0
570	843	48.3	0.636	— 382.3
600	873	76.9	1.012	— 10.05
632	905	113.3	1.490	360.4
681	— 954	203.9	2.754	966.3
723	996	325.4	4.282	1448
742	1015	417	5.486	1727
752	1025	458	6.027	1841

Melting began at 563° C. when the vapour pressure was 0.59 atmospheres, but the final melting-point was not observed. According to the old theory, it would be expected that the stable modification would melt at a higher vapour pressure than *any* shown by the metastable form, since the liquidous curve is supposed to have increasing values of the vapour pressure as the temperature rises. Actually, however, the vapour pressure at the initial melting-point was much lower in this case. These facts were explained on Smits' theory of allotropy.

CHAPTER XXIII.

THE INFLUENCE OF TRACES OF OTHER CATALYSTS ON THE PHYSICAL PROPERTIES OF LIQUIDS.

ALTHOUGH not falling strictly within the scope of this subject, no account of the influence of traces of moisture on physical properties would be complete without comparing the effects observed with two other closely related phenomena. These are the pronounced influence on physical properties which can be exerted by traces of catalysts other than water, and the influence which subjection to an electrical field appears to have on physical properties.

With the object of throwing some light on the question of the equilibrium between complex and simple molecules in a liquid, Baker¹ carried out experiments with the object of finding out whether catalysts other than water had any disturbing influence on this equilibrium. Two methods of attack were adopted, the determination of the vapour pressure and the measurement of the surface tension.

In the first series of experiments on vapour pressures, charcoal was used as the catalyst. Barometer tubes were made of hard Jena glass, one end of which dipped under mercury. The upper ends were furnished with bulbs in which very pure sugar charcoal could be heated to redness while the tube was being exhausted. After admission of the liquid, the tube connecting the bulb with the pump was sealed off, and the tubes were surrounded by a jacket of circulating water.

The results of these preliminary experiments showed that the presence of charcoal did exert an influence on the vapour pressure. With ether at 16°, the vapour pressure was 25 mm. greater than with the liquid alone. With methyl alcohol, at 18° the vapour pressure was 6 mm., and at 35°, 12 mm. greater in the presence of the catalyst. With benzene, the increase was 2 mm. only, and this excess of vapour pressure was unaltered whether the temperature was 23° or 37° C.

¹ *J. Chem. Soc.*, 1927, 949.

It was found, however, that quantitative measurements of the vapour pressures of each of the liquids showed considerable variations. Similar results were obtained on using the two methods devised by Smith and Menzies,¹ even when the same liquid and the same catalyst were used in successive experiments. Some of the results so obtained are given in Fig. 41.

One fact definitely established was that a catalyst in a liquid acts very slowly, and in some cases at first even in a contrary direction to that shown in the final equilibrium. That is, in any liquid there is a balance between the large and small molecules, for in all ten liquids examined there was some evidence of associa-

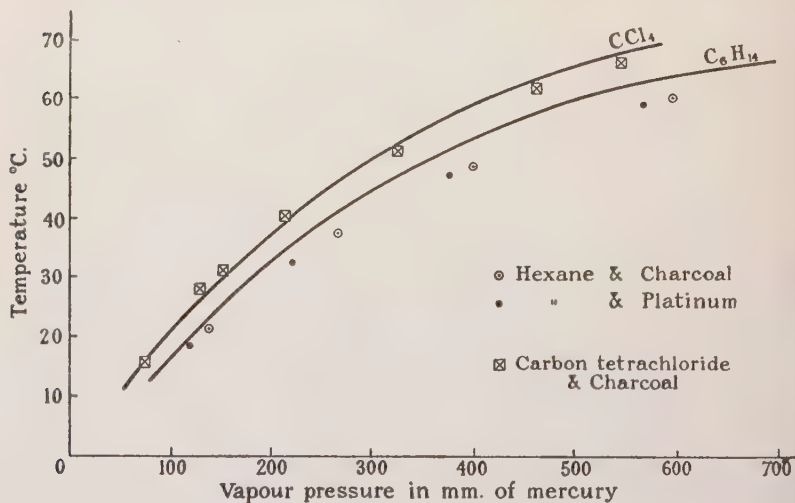


FIG. 41.

tion. The presence of certain catalysts can influence the equilibrium, under different temperature conditions, in the direction of producing more complex molecules, and so lowering the vapour pressure, and then, under different conditions, especially long time of contact, may produce increased dissociation and higher vapour pressure.

The second difficulty encountered was that a pure liquid appeared to have no constancy in its composition; e.g. pure bromine, without any catalyst, gave vapour pressures which showed considerable variations according to the history of the particular specimen. If bromine were boiled for some time and the measurement taken as soon afterwards as possible, it was

¹ *J. Amer. Chem. Soc.*, **32**, 907, 1412 (1910).

found that the vapour pressure was very sensibly higher than it had been before the boiling took place. The recovery of the old vapour pressure was quite slow, and many days elapsed before the effect of the boiling had disappeared.

To eliminate this effect, the vapour pressure was balanced against the pressure of the liquid with the catalyst through a pressure gauge, as shown in Fig. 42. To each of the upper ends of a *U*-shaped tube containing mercury was sealed a pair of bulbs, which were connected with each other by a capillary tube. Into one bulb was introduced the catalyst, and the liquid was placed in the second of the pair. The same liquid was then introduced into one of the bulbs of the other pair, the second one being left empty. All the entrance tubes but one were sealed off. The remaining tube was connected to a "Hyvac" pump. The liquid in the two bulbs was allowed to boil into the evacuated space in order to remove dissolved air; the liquid was then frozen and the bulb containing the catalyst suitably heated for the same object. The tube connected with the pump was now sealed off, and the apparatus allowed to stand for an hour. Finally the capillary tube connecting the two sets of bulbs was sealed with a fine pointed flame. On transferring the apparatus to a thermostat, it was found that the mercury level in both limbs of the *U*-tube was the same, showing the apparatus to be in order. By cooling the bulb containing the catalyst, the liquid was distilled over from the adjoining bulb. Thus the two lots of liquid could be treated in exactly the same way, and a direct determination could be made of the difference in vapour pressure brought about by the catalyst. The results are shown in Table XLV.

In each system there was an increase in the vapour pressure of the liquid in contact with the catalyst over the vapour pressure of the liquid alone. This difference increased with time up to a certain point and then became constant. The effect of the increase of vapour pressure produced by a catalyst was always seen with this apparatus, for, on standing, the liquid evaporated away from the catalyst and condensed in another part of the

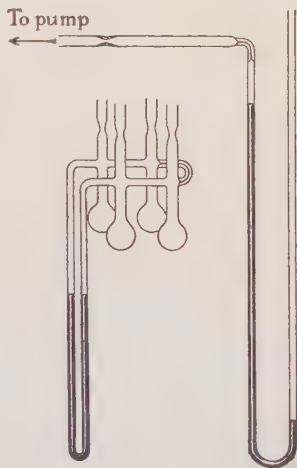


FIG. 42.

FIG. 43.

apparatus, although the whole was kept at a constant temperature.

TABLE XLV.

Acetic Acid and Charcoal.		Acetic Acid and Platinum Black.		Acetic Acid and Thoria.	
Time.	Diff. mm. Hg.	Time.	Diff. mm. Hg.	Time.	Diff. mm. Hg.
Day of sealing .	2.15	Day of sealing .	0.3	Day of sealing	0.4
2 days later .	1.5	1 day later .	0.25	3 weeks later .	0.25
After heating at 80° 4 hrs. .	2.95	After heating at 80° 4 hrs. .	0.5	3 weeks later .	1.27
6 days later .	2.0	1 day later .	0.75	Heated at 90° for 4 hrs. .	1.32
After keeping at 15° 24 hrs. .	2.05	6 days later .	0.8		
2 days later .	2.4	After cooling at 15° 1 day .	1.05		
5 months later	1.9	3 days later .	1.6		
		After heating at 90° 4 hrs. .	1.75		
		5 months later	2.2		

Benzene and Nickel.	Methyl Alcohol and Charcoal.	Ether and Charcoal.
Difference in mm. Hg.	Difference in mm. Hg.	Difference in mm. Hg.
3.4	5.5	40.0
3.3	6.3	41.3
3.3	6.2	41.2
3.5	6.5	39.2
3.1	6.1	40.2

BROMINE AND CHARCOAL.

Time.	Diff. in mm. H ₂ SO ₄ satd. with Bromine.	Time.	Diff. in mm. H ₂ SO ₄ satd. with Bromine.
Initial Difference .	38.5	Interval of 2 days .	95.2
Interval of 2 days .	50.9	" " 14 " .	125.1
" " 1 day .	51.7	" " 16 " .	133.75
" " 1 " .	52.8	" " 3 " .	142.3
" " 6 days .	85.2		

The effects of heating and cooling on this difference of vapour pressure were tested, and it was found that heating increased the difference, whilst cooling diminished it. On standing, however, the original value of the difference was restored, although in some cases the time needed was some weeks.

In order to investigate the effect of heating on the vapour pressure of the liquid alone, as well as in the presence of catalysts, an improved barometer tube method was used. The tube, Fig. 43, was *U*-shaped, and made of Jena glass. The upper end of one limb was bent into a horizontal position, and by drawing it out to a capillary, a bulb was formed about two inches in length, to hold the catalyst. The liquid was introduced into the main barometer tube, and the catalyst into its bulb. The tube was then evacuated through the capillary, and after the liquid had been allowed to boil to expel dissolved air, the part of the vertical tube containing it was frozen, and the catalyst was heated. In order to give the charcoal the same state of activity in successive experiments, it was heated to 450° for an hour and a half, the pump being kept running. The capillary was then sealed, and the tubes transferred to a large glass-sided thermostat.

TABLE XLVI.

ACETIC ACID.

Catalyst.	Before Heating.	Heated at 80° for 24 hours, then cooled to 20° .	One week after heating at 20° .
None	Normal	+ 2 mm.	Normal
Charcoal	+ 1.8 mm. After an interval of 6 weeks + 6.0 mm.	+ 2.3 "	+ 6.8 mm.
Thoria	+ 0.65 mm. After an interval of 6 weeks + 7.3 mm.	+ 1.5 "	+ 7.3 "
Platinum	+ 2.72 mm. After an interval of 6 weeks - 1.2 mm.	- 3.8 "	+ 1.1 "

WATER.

Catalyst.	Before Heating.	Heated at 80° for 48 hours, then cooled to 20° .	Two weeks after at 20° .
None	Normal	Normal	Normal
Charcoal	+ 2.5 mm.	+ 4.3 mm. 1 day later + 0.75 mm.	+ 2.5 mm.
Thoria	+ 2.4 "	+ 4.0 mm. 1 day later + 1.2 mm.	+ 0.9 "
Platinum	+ 1 "	+ 3.2 mm. 1 day later + 0.6 mm.	+ 0.5 "

Measurements of the vapour pressure of water in the presence of the catalysts charcoal, platinum, and thoria showed that in each instance heating has the same ultimate effect, but the interval between the actual heating and the appearance of the effect

of the heating varies with the different catalysts. With thoria and platinum, heating at 80° for twenty-four hours produced an increase in vapour pressure at ordinary temperatures, but if the time of heating were prolonged to forty-eight hours, the vapour pressure within twenty-four hours of heating showed a decrease from the constant value, this decrease disappearing if the tubes were allowed to stand for a few days at room temperature.

The charcoal and water, when heated at 80° C. for twenty-four hours, showed an increase in vapour pressure, if the readings were made within twenty-four hours of the heating. This low value slowly changed back to the constant value when the barometer tubes containing the water and charcoal were allowed to stand for a few days at the ordinary temperature.

With acetic acid, charcoal as catalyst produced a decrease after twenty-four hours' heating; after seventy-two hours' heating, there was a decrease which temporarily increased for a day or two, the normal value finally returning. Thoria caused a decrease in vapour pressure when heated with acetic acid, the amount of the decrease being greatest a day or two after the heating had taken place. With platinum, a diminution in vapour pressure was caused by the heating, the normal value returning after a short while.

Surface Tension.—Experiments were also carried out to determine the molecular weights of some liquids by the method of Ramsay and Shields. The catalysts and liquids were from the same preparations as those used in the vapour pressure experiments. In all cases comparative tubes were used containing the liquid alone, without the presence of any catalyst, so that a direct estimation of the effect of the catalyst could be made under various conditions of temperature, etc.

It was found that a catalyst does not seem to produce its maximum effect on the complexity of the molecules at once. This is seen from Table XLVII.; the temperature interval was about 20° , the higher temperature being 40° C.

The table for acetic acid alone shows that the acid does not reach its normal value in two days after filling. This points to the conclusion that in the process of filling the tube, which involves the boiling of the liquid for some time to get rid of air, dissociation of the molecules of liquid takes place, and that in three weeks the normal molecular weight is restored. With charcoal, the same phenomenon was observed, but the molecular weight was greater by 24, with platinum black it was greater by 52, and with thoria 29.

TABLE XLVII.

Acetic Acid and Charcoal.		Acetic Acid alone.	
Time.	Mol. Weight.	Time.	Mol. Weight.
After 1 day . .	1·541 × 60	After 1 day . .	1·546 × 60
„ 2 days . .	1·952 × 60	„ 2 days . .	1·568 × 60
„ 3 weeks . .	2·525 × 60	„ 3 weeks . .	2·097 × 60
„ 12 months . .	2·492 × 60	„ 9 months . .	2·097 × 60
Acetic Acid and Platinum Black.		Acetic Acid and Thoria.	
Time.	Mol. Weight.	Time.	Mol. Weight.
After 2 weeks . .	2·40 × 60	After 1 day . .	2·538 × 60
„ 3 months . .	2·273 × 60		
„ 8 „ . .	2·976 × 60		

Similar effects were shown by water, as shown in Table XLVIII.

TABLE XLVIII.

Water and Platinum.		Water and Thoria.	
Time.	Mol. Weight.	Time.	Mol. Weight.
Day of filling . .	3·352 × 18	3 weeks	3·125 × 18
After 6 months . .	4·442 × 18	5 „	3·612 × 18
Heated at 40° for 16 hrs. . . .	3·948 × 18	9 „	3·866 × 18
1 week later . .	3·713 × 18		
2 weeks later . .	3·047 × 18		
1 day later . .	2·915 × 18		

Ramsay and Shield's value for this temperature interval is $3·259 \times 18$.

This method has the disadvantage that the heating, even only to 40° C., seemed to disturb the equilibrium, and this was not restored at once on cooling at ordinary temperatures. Hence the effect of temperature was studied on the constitution of these liquids in the presence and absence of catalysts. After heating or cooling, the liquids were allowed to stand at the ordinary temperature for the time specified, so the effects shown are those not measured at the high or low temperature, but through the interval 17° to 40° C.

TABLE XLIX.

ACETIC ACID.

Catalyst.	Before Heating.	After Heating at 80° for 2 hours.	After Heating at 80° for 48 hours.	After 24 hours at the ordinary Temperature.
None . . .	2·168 × 60	2·32 × 60	1·97 × 60	1·666 × 60
Platinum black .	1·872 × 60	2·527 × 60	1·782 × 60	1·586 × 60
Charcoal . . .	2·492 × 60	2·552 × 60	1·690 × 60	2·490 × 60
Thoria . . .	1·992 × 60	2·538 × 60	2·218 × 60	2·452 × 60

Except in the cases of bromine alone and acetic acid with charcoal, heating for only a short period seemed to increase the molecular complexity, whilst heating for a long period decreased it, as would be expected. The recovery to normal was slow, but even after three days' standing at the ordinary temperature the molecular weight was often considerably above or below that at the beginning of the experiments.

The agreement between vapour pressure and surface tension results was not quantitative. Baker considers that this could not be expected, since, by the surface tension method, the average complexity of the molecules was estimated, whilst vapour pressure largely measured that of the smaller molecules present.

Baker concluded that all liquids may be regarded as analogous to a dissociable gas such as nitrogen tetroxide. At low temperatures the heavy molecules are more numerous; at higher temperatures the lighter ones predominate, and dissociation and combination are probably both increasing. Liquids, however, are supposed to differ in that dissociation and association are much slower in liquids than in gases. Equilibrium in liquids may be profoundly disturbed by even a comparatively slight change of temperature, and complete recovery of the normal condition may be a matter of weeks or even months.

Density.—Preliminary results have been published by Peel, Robinson, and Smith¹ of experiments which indicated that a considerable change in density occurs when water and ether are brought into contact with catalysts. The results are shown in Table L.

Thus with a higher temperature there is a greater initial drop in the case of thoria and water, but the difference between the highest and lowest values is about the same as at the lower temperature.

¹ *Nature*, **120**, 515 (1927).

TABLE L.

Liquid.	Catalyst.	Temperature.	Density Change.	Time.
Water	Carbon	14.1° C.	+ 0.000080	48 hours
			+ 0.00019	96 "
			+ 0.00020	150 "
			(equilibrium value)	
Ether	Carbon	14.8° C.	+ 0.0009	18 hours
			+ 0.0011	42 "
			+ 0.0013	90 "
			+ 0.0013	130 "
Water	Thoria	18.5° C.	- 0.00017	24 "
			- 0.00002	48 "
			+ 0.00001	96 "
			+ 0.00011	192 "
		23.3° C.	+ 0.00015	209 "
			- 0.00040	24 "
			+ 0.00004	209 "

Summary.—When liquids are sealed in bulbs with insoluble solid catalysts, remarkable changes gradually occur in the physical properties of the liquids. These changes have been recorded in the cases of vapour pressure, surface tension, and density. They are attributed to changes in the molecular complexities of the liquids concerned, consequent on a shift in the inner equilibrium between the larger and simpler molecules. This shift occurs very slowly, and in some cases at first even in a contrary direction to that shown in the final state.

CHAPTER XXIV.

THE APPARENT INFLUENCE OF AN ELECTRIC FIELD ON THE PHYSICAL PROPERTIES OF LIQUIDS.

WORKING on the basis of J. J. Thomson's Theory (see p. 142), Baker¹ presumed that it should be possible, even in the presence of water, but in the absence of facilities for its condensation into

drops, to stabilise the large molecules and increase the number of them above the normal number corresponding to a given temperature.

Hence hexane, benzene, and carbon disulphide were dried in so far as concentrated sulphuric acid could do so, i.e. a large number of water molecules remained, diffused through the molecules of the liquid. Tubes of 1 cm. diameter were prepared, with two platinum plates, about 7 cm. long, fixed facing each other at the lower end of the tube. A thermometer was placed between them. Benzene was introduced just to cover the plates (Fig. 44). By connecting the platinum plates with a

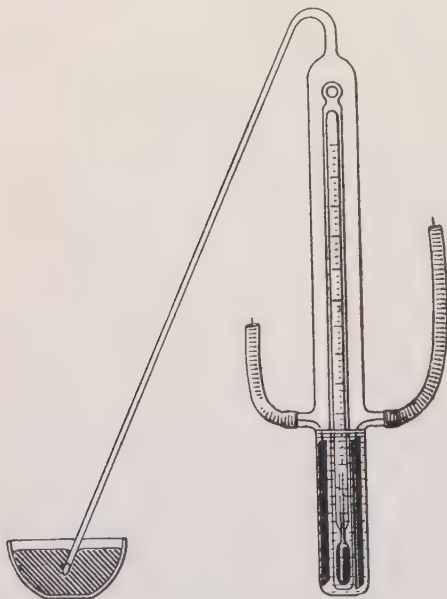


FIG. 44.

400 volt battery for some time, the boiling-point of the benzene was raised to 91° . A precisely similar tube containing the same benzene and similar electrodes, but without the applied voltage, was placed in the same bath; the benzene boiled at 79.6° . The

¹ *J. Chem. Soc.*, 1928, 1051.

effect was not destroyed when the apparatus stood for a few days with the plates disconnected from the battery ; the boiling-point was 88° and boiling was steady, not violent. While the boiling was proceeding, the voltage was again applied, and in two minutes the evolution of bubbles stopped. Surface tension measurements indicated a molecular weight between two and three times that corresponding to the formula C_6H_6 . Similar results were obtained with hexane and carbon disulphide.

Baker explained the phenomenon by supposing the ions to be removed by the electric field, and therefore the water present was incapable of collecting into drops. Not a trace of gas could be collected over the mercury in the trough, so the effect did not appear to be due to the elimination of water by electrolysis, and consequent drying of the liquid. Moreover, if the plates were connected together and allowed to stand, the surface tension indicated a normal molecular weight, and the normal boiling-point was restored.

Smits, however, has cast some doubt on whether the effect observed by Baker was due to a change in the internal complexity of the liquid. He repeated Baker's experiment.¹ Before the platinum plates were connected with the 400 volt battery, the boiling-point of the benzene was 80.5° , and after the current had passed for four hours, it had risen to 95° , but fell to 88° under steady boiling. The bubbles originated from a small part of the platinum wire fixed to one of the plates. The electrodes were connected together, and after two days the boiling-point without again applying an electric field was 93° , but sank to 88° under steady boiling. On heating directly with a small flame, however, the benzene boiled at 80.5° , and Baker's phenomenon disappeared entirely. Hence his high boiling-points may be affected to an unknown degree by superheating. At the same time it was shown that the vapour pressure was exactly the same (a) without the field ; (b) with applied field of 400 volts ; (c) with applied field of 800 volts. Hence Smits concludes that the electric field does not effect any change in the inner equilibrium, and that the increase in the boiling-point is probably due to the removal of electrically charged dust particles by the field, in which case superheating occurs more easily when heating is carried out in a bath.

It was further concluded that since abnormal surface tensions were obtained, it seems most probable that if a liquid by long standing in a sealed tube has become free from dust particles,

¹ *J. Chem. Soc.*, 1928, 2399.

the surface tension may be changed, and it is hence no longer a trustworthy criterion as to the state of the inner equilibrium in a liquid.

This work has been repeated by the author,¹ the results obtained being in complete agreement with those of Smits. No change could be observed in the vapour pressure either when a mercury manometer was used or with a glass spring indicator, although electric fields were applied up to about 1500 volts per cm. and the temperature of measurement was varied from 0° C. to 80° C. Similarly, after a fraction of the benzene had been removed by condensation, the rate of attainment of the previous vapour pressure was almost exactly the same as when a fraction was removed under similar conditions before the application of the field. This behaviour contrasted strongly with that of intensively dried liquids, in which the rate of attainment of a constant vapour pressure is extremely slow.

On the other hand, the boiling-point as determined by heating the bulb containing the liquid in an oil bath was invariably considerably above 80° C., but the vapour temperature remained constant at 80°.

The only possibility which remained seemed to be that the "dead space" behind and at the side of the electrodes was of importance, since much lower boiling-points were observed when this "dead space" was considerable. In order to eliminate this, a new type of cell was used, consisting of a flat bulb with parallel sides about 7 mm. apart and with platinum wires sealed through each face. These faces were then silvered on the inside so as to form two parallel silver plates. Again with this type of apparatus no vapour pressure change was observed on connecting to a potential difference of 440 volts for a month. Boiling-point determinations with such a cell served to throw some light on this phenomenon however. After applying an electric field for two or three days the apparent boiling-point of the benzene, as indicated by a thermometer in the liquid, was raised very considerably. The heating, as before, was carried out by means of an oil bath, and on some occasions the temperature could be raised to 104° C. before ebullition commenced. This occurred suddenly, and the temperature fell through a few degrees, after which the liquid boiled quite steadily at a temperature of about 96° C. If, however, either when this steady ebullition was occurring, or when the liquid was at some slightly lower temperature, the liquid was stirred vigorously with the thermometer,

¹ J. W. Smith, *J. Chem. Soc.*, 1929, 788.

bubbles of vapour escaped violently from the liquid in the tube and the temperature fell. As soon as agitation was discontinued the ebullition ceased and the temperature began to rise again. The more vigorously the liquid was stirred, the lower the temperature became.

One experiment of Baker's which it was not found possible to reproduce was the steady rise in the temperature of the boiling liquid after the field had been applied to the fresh benzene. This boiled in the bulb heated by an oil bath at 80.5°C. , and no rise in this boiling-point could be observed after application of the field for four hours. Thus it was concluded that the agitation caused by the ebullition destroyed the effect which the electric field tended to produce.

The observation of Smits that the boiling-point when determined by direct heating of the bulb with a micro-burner was quite normal, was also confirmed.

Thus it appears almost certain that Baker's observation of a rise in the boiling-point after application of an electric field was due to superheating induced by the removal of charged nuclei from the system.

A similar conclusion has also been reached by Lenher,¹ who finds that the boiling-point of benzene subjected to a direct current potential of 450 volts for over twenty-four hours remains unchanged when heating is carried out with a platinum wire heating element, whilst when a heating bath is used superheating readily occurs.

¹ *Nature*, **123**, 907 (1929).

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
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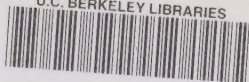
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